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Fourth EC-JRC aromatic compounds inter-laboratory comparison with automatic analysers

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Abstract

This report presents the results of the fourth inter-laboratory comparison for BTEX automatic analysers performed at the JRC Ispra from the 19th to the 22nd of September 2016. Twelve national reference laboratories with fourteen instruments participated in this exercise. Six concentration levels were tested during the inter-laboratory comparison. Benzene concentrations ranged from 1 to 50 µg/m^3. The exercise was evaluated according to ISO 13528 methodologies for the evaluation of inter-laboratory proficiency assessment and the recommendation of the protocol N37 of the AQUILA network. Participating laboratories are identified as requested by the AQUILA protocol.

The report, compares reference and robust average values for the concentrations tested during the exercise, gives information on the technique and instrumentation used by each participant and shows the results of linearity tests, identification of outliers, repeatability, reproducibility and robustness of the methodology, and also parameters to evaluate laboratory results: repeatability score, bias and E_n values.

In general, the results showed a relative improvement with respect to the previous inter-laboratory exercises from 2013. This was mainly reflected in the inter-laboratory exercise reproducibility values of the C8 compounds (ethyl-benzene and xylenes). Repeatability and reproducibility values for benzene and toluene were approximately 4 % and 9 %, providing consistent robust values. Ethyl-benzene, m,p-xylene and o-xylene showed higher variability with repeatability values ranging from 6 to circa 7.5 % and reproducibility values between 12 and 14 %.

1 Introduction

This BTEX inter-laboratory comparison exercise was the fourth exercise carried out by the Joint Research Centre aiming to fulfil the QAQC programme for the harmonization of air quality measurements in Europe in accordance with the Directive 2008/50/EC.

Following on from previous exercises, this comparison focussed on the performance of laboratories to measure the analytes of interest over an established range of concentrations.

The inter-laboratory comparison was carried out at the JRC Ispra site bench facility from 19th to 22nd September 2016. Participants were required to register and provide a detailed description of their instrumentation.

Measurement results were evaluated according to the repeatability-score and the E_n value. The report also provides additional information regarding linearity test, blank level and overall repeatability and reproducibility values. As agreed within the AQUILA protocol participating laboratories have been identified in this report.

2 Inter-laboratory comparison strategy

The reporting of results from the participating laboratories was done by uploading the requested information on the JRC web site application at http://interlabo-comparison.jrc.ec.europa.eu. This included the characteristics of the BTEX analyser, description of the calibration method and traceable reference material. 30 min average concentrations and their corresponding associated uncertainties to characterise each 90 min step concentration interval were also requested. The reported information from the participants is shown in the annex: Relative standard deviation, analytical uncertainty and uncertainty of the concentration level calculated for each laboratory.

The exercise consisted of a zero air check and an up and down of six concentration level steps of two hours each. This time interval allowed the different automatic analysers, according to their modus operandi, to perform three or six complete measurements of 15 or 30 minutes, respectively. The time schedule for the exercise is given in the annex: Work schedule for the inter-laboratory comparison exercise.

In this exercise, concentrations were expressed in $\mu g/m^3$ at 20 °C and 1 atm. Conversion factors from ppb (v/v) to $\mu g/m^3$ for reporting results were agreed before the inter-laboratory comparison (see annex: Conversion factors for data reporting).

2.1 Participating laboratories and instrumentation

Twelves NRLs participated in the inter-laboratory comparison exercise. Table 1 shows the name of the participating laboratories. HMS and VMM reported results from two different instruments.

Table 2 identifies the type of instrumentation used by each laboratory. Of the fourteen instruments used during this exercise, five had a flame ionization detector (FID), while the others used a photo ionization detector (PID). Table 3 shows the reference material or travelling standard used by each laboratory to calibrate their analysers.

Table 1. List of participating laboratories

Acronym	Laboratory	Country	Contact
HMS	Air Quality Reference Centre, Hungarian Meteorological Service	Hungary	Viktor Dézsi, Attila Machon
ISCIII	Instituto de Salud Carlos III	Spain	Rosalía Fernández Patier, Pilar Morillo , María Rodríguez
DLI	Air Quality Section Department of Labour Inspection Ministry of Labour and Social Insurance	Cyprus	Christos Kizas, Christos Papadopoulus
EKONERG	Energy and Environmental Protection Institute	Croatia	Predrag Hercog, Marijo Bilic
EEA	Executive Environmental Agency	Bulgaria	Milena Parvanova, Nikolay Panayotov
VMM	Vlaamse milieumaatschappij	Belgium	Sarah Decoux, Jan Petré
EPA	Environmental Protection Agency	Ireland	Lin Delaney, Patrick Malone, Micheál O'Dwyer
REE	Ricardo Energy and Environment	United Kingdom	James Dernie, Pedro Abreu
LIKZ	Ambient Air Testing Laboratory Croatian Hydrological and Meteorological Service	Croatia	Lovro Hrust, Lukša Kraljevic'
AAA	Environmental Protection Agency	Lithuania	Juozas. Molis, Tomas Gaižutis
CHMI	Calibration Laboratory of Immission Czech Hydrometeorological Institute	Czech Republic	Miroslav Vokoun, Jan Silhavy
LCSQA	Laboratoire Central de Surveillance de la Qualité de l'Air. Mines Douai – Départment Sciences de l'Atmosphére et Génie de l'Environnement (S.A.G.E.)	France	Nadine Locoge, Thierry Leonardis

Table 2. Instrumentation used by the participants during the inter-laboratory comparison exercise

Code	Analyser	Cycle time, min	Detector	Column: Length, i.d.*, film thickness Operational conditions	Adsorbent, Sampled volume Desorption conditions
HMS-1	CHROMATOTEC AIRMOTEC, AIRMO VOC C6-C12, A3100, (2003)	30	FID	MXT30CE: 30 m, 0.28 mm, 1 µm 36°C,2°C/min, 38°C,2°C/min, 50°C,10°C/min, 80°C,15°C/min, 200°C	Carbotrap-B, 415 ml 380°C for 240 s, 3 ml/min
HMS-2	Environment SA VOC 72 M (2014)	15	PID	Stainless Steel: 15 m, 0.25 mm, 1 µm 25°C,5°C/min, 30°C(60 s),15°C/min, 115°C(420 s),30°C/min, 160°C(120 s)	Carbotrap-B, 165 ml 380°C for 120 s, 12 ml/min
ISCIII	SYNTECH SPECTRAS Analyser GC 955, 2004	15	PID	AT-624: 13 m, 0.32 mm, 1.8 µm 50°C (3'),10°C/min,70°C (6 s), -10°C/min,50°C	Tenax GR, 50 ml 180°C for 40 s, 1.5 ml/min
DLI	SYNSPEC Analyser GC 955 Vers. 600, (2008)	15	PID	AT-5 :13 m, 0.32 mm, 1 µm 50°C (3-4 min), 80°C (12 min)	Tenax GR (60/80 mesh) 180°C for 15-60 s, 1.4 ml/min
EKONERG	Chromatotec AirmoVOC GC866 (2014)	15	FID	MXT30CE 30 m, 0.28 mm, 1 µm 44°C,2°C/min, 45°C,15°C/min, 165°C(360s)	Carbotrap, 470 ml 80°C for 120 s
EEA	Environment S.A. VOC72M (2013)	15	PID	n.a.** : 15 m, 0.25 mm, 1 µm 25°C,5°C/min, 30°C(60 s),30°C/min, 160°C(120 s)	Carbotrap-B, 165 ml 380°C for 60 s, 15 ml/min
VMM-1	SYNSPEC Analyser GC 955, Vers. 601 (2013)	15	PID	AT-624: 13 m, 0.32 mm, 1 µm 50°C (3 min),10°C/min,70°C (7 min)	Tenax GR, 140 ml 180°C for 60 s, 1.5 ml/min
VMM-2	Chromatotec GC866 Vers A31022 (2011)	15	FID	MXT30CE: 30 m, 0.28 mm, 1 µm 45°C (60 s),2°C/min, 165°C (480 s)	Carbotrap-B, 450 ml 380°C for 120 s, 3-4 ml/min
EPA	SYNTECH Analyser GC 955, Vers. 600, 2008	15	PID	AT-5, 13 m, 0.32 mm, 1µm 45°C (240 s),14°C/min, 80°C (1 min)	Tenax GR 35/60, 210 ml 180°C for 60 s, 1.5 ml/min
REE	Environment S.A. VOC71M (2011)	15	PID	SPB-624: 13 m, 0.32 mm, 1.8 µm 34°C (115 s),20°C/min,150°C (155 s)	Carbopack-B, 900 ml 340°C for 180 s, 1 ml/min
LIKZ	SYNTECH SPECTRAS Analyser GC 955 Vers. 601, (2013)	15	PID	CP7003: 13 m 50°C (3 min),10°C/min,70°C (7 min)	Tenax GR, 93 ml 180°C
AAA	AMA Instrument, CG5000 BTX FID, VERS 3, 2011	30	FID	AMAsep1, 30 m, 0.32 mm, 1.5 µm 50°C (180 s),8°C/min,130°C (5')	Carbotrap, 300 ml 230°C for 180 s, 2 ml/min
CHMI	Environment S.A. VOC71M (2005)	15	PID	EPA-624: 13 m, 0.32 mm, 1 µm 42°C (120 s), 3°C/min,45°C, 17.5°C/min,150°C (195 s)	Carbotrap/Carbopack-B , n.a. 350°C for 180 s, 4 ml/min
LCSQA	Chromatotec VOC C6-C12 (2008)	15	FID	Metalic Column: 30 m, 0.28 mm, 1 µm 36°C (1 min),2°C/min,38°C, 10°C/min 68°C, 15°C/min, 200°C (4 min)	Carbotrap, 920 ml 380°C for 240 s, 3.5 ml/min

* i.d.: internal diameter
** not available

Table 3. Reference material used by the participating laboratories

Laboratory	Reference Material	Benzene ppb(m/m)	Toluene ppb(m/m)	Ethyl-benzene ppb(m/m)	m-Xylene ppb(m/m)	p-Xylene ppb(m/m)	o-Xylene ppb(m/m)	Other Comp.	Producer	Certified by	Certification date
HMS	Press. Cyl. D.D. (Environics 200)	965±29	990±29	969±29	979±29	983±29	996±30	-	VSL	VSL	n.a.
ISCIII	Press. Cyl. D.D. (API model 700)	503±15	501±15	505±15	498±15	504±15	491±15	-	VSL	VSL	04/11/2015
DLI	Press. Cyl. D.D. (Dilutor Sabio 4010)	677±20	675±20	680±20	670±20	679±20	661±20	-	VSL	VSL	04/06/2015
EKONERG	Press. Cyl.	12.14±0.24	12.30±0.31	11.61±0.29	12.21±0.31	11.75±0.30	12.28±0.31	_	NPL	n.a.	n.a.
EEA	Pres. Cyl.	10.00±0.60	--	---	---	---	---	_	SIAD Italy	SIAD Italy	n.a.
VMM	Press. Cyl. D.D. (AirQrate)	196.5±3.9	196.6±4.9	195.9±4.9	199±5		199±5	-	NPL	NPL	9/04/2016
EPA	Press. Cyl.	10.11±0.20	10.24±0.26	9.67±0.25	19.93±0.50		10.23±0.26	-	NPL	NPL	25/09/2015
REE	Press. Cyl.	5.93 ± 0.08	4.01±0.08	4.05±0.08	3.99±0.08	4.02±0.08	4.03± 0.08	-	NPL	NPL	11/03/2009
LIKZ	Press. Cyl. D.D. (Teledyne API T700)	100.9±2	102.2±2	96.4±2.5	198.9 ±5.0		102.1±1.6	-	NPL	NPL	03/09/2015
AAA	Press. Cyl. DD. (Umwelttechnik MCZ)	4990±100	5110±0.100	-	-	-	-	-	NPL	NPL	16/12/2009
CHMI	Press. Cyl. S.D. Canisters	10,1±0.2	10.1±0.2	9.81±0.2	19.87±0.5		10.06±0.2	30 H.C. MIX.	NPL	NPL	13/08/2014
LCQA	Press. Cyl.	14.00±0.16	13.53±0.16	12.92±0.16	13.82±0.20	13.69± 0.20	13.26±0.19	-	Messer	LNE	06/09/2016

Press. Cyl.: Pressurised cylinder; D.D.: Dynamic Dilution; H.C.: Hydrocarbons; n.a.: not available; P.T.: Permeation Tubes; S.D. Canisters (Static Dilution injection in canisters).
ppb(m/m): concentration in part per billion with respect to molar fraction ± its expanded uncertainty (k=2)

2.2 Reference values

A GC Agilent 7890A coupled with an on-line sampling Thermal Desorber Unity2 from Markes was used by ERLAP to trace the concentrations during the exercise. This instrument was calibrated against reference material (NPL Primary reference gas mixture: Reference 2016040285) by a multipoint calibration over the operative concentration range of the exercise (annex: Analysers and method description from participating laboratories ERLAP). The uncertainty of the reference concentration corresponded to the analytical uncertainty derived from the ERLAP measurements carried out during the comparison. Reference concentrations and calculated uncertainties for each level of concentration are given in Table 4 and annex: Uncertainty of the reference value and overall inter-laboratory results.

Table 4. Reference values and associated uncertainties of the exercise

Level	Benzene Conc., µg/m^3	uncertainty (1σ) %	Toluene Conc., µg/m^3	uncertainty (1σ) %	Ethylbenzene Conc., µg/m^3	uncertainty (1σ) %
1ST-A	1.44	5.37	3.27	4.82	0.87	10.31
2ND-A	3.02	2.59	10.92	1.62	2.18	1.92
3RD-A	5.29	1.24	19.52	0.87	3.79	2.11
4TH-A	10.38	1.11	39.09	1.18	7.30	1.37
5TH-A	31.37	0.69	118.56	0.68	21.80	1.03
6TH-A	52.31	0.67	190.57	0.90	35.26	0.94
5TH-B	31.32	0.99	119.24	1.01	22.09	0.76
4TH-B	10.62	1.20	40.57	0.91	7.71	1.32
3RD-B	5.38	0.96	20.33	0.79	3.92	1.16
2ND-B	3.10	1.18	11.58	1.23	2.28	1.84
1ST-B	1.49	2.97	3.84	3.13	0.95	5.56

Level	m,p-Xylene Conc., µg/m^3	uncertainty (1σ) %	o-Xylene Conc., µg/m^3	uncertainty (1σ) %
1ST-A	1.08	12.94	0.88	13.21
2ND-A	2.41	4.56	2.32	2.88
3RD-A	4.17	2.32	4.11	1.24
4TH-A	7.91	1.50	7.98	0.97
5TH-A	23.71	1.20	23.84	0.73
6TH-A	38.37	1.29	38.78	1.09
5TH-B	24.18	1.29	24.12	0.88
4TH-B	8.49	1.46	8.44	1.32
3RD-B	4.36	2.32	4.35	1.65
2ND-B	2.61	3.83	2.52	2.89
1ST-B	1.18	9.85	1.04	5.52

2.3 Statistical considerations

2.3.1 Average concentration and uncertainty

The three concentrations, $C_{n,\Delta t}$, and associated uncertainties, $u_{n,\Delta t}$, were averaged in order to determine the concentration, $\overline{C}_n$, and associated expanded uncertainty, U_n, at each concentration step, n:

$$\overline{C}_n = \frac{C_{n,0-30\min} + C_{n,30-60\min} + C_{n,60-90\min}}{3}$$

Eq. 1

$$U_n = \sqrt{\frac{\left(C_{n,0-30\min} - \overline{C}_n\right)^2 + \left(C_{n,30-60\min} - \overline{C}_n\right)^2 + \left(C_{n,60-90\min} - \overline{C}_n\right)^2}{3} + 4 \cdot \left(\frac{u_{n,0-30\min}^2 + u_{n,30-60\min}^2 + u_{n,60-90\min}^2}{3} \right)}$$

Eq. 2

These values were used for the inter-laboratory comparison and are reported in Table 10 to Table 14, where the expanded uncertainty, U_n, is expressed as percentage of its referred concentration, U %.

2.3.2 Linearity test

Linearity of the analysers was tested according to EN14662-3 by comparing the average value of the reported results at each level and instrument, $\overline{C}$, with its respective reference value, Cref , at this level. Residual, Rc, is calculated according to the following expression:

$$R_c = \overline{C} - (a + b \cdot C_{ref})$$

Eq. 3

where a and b are the correlation coefficients of the corresponding linear regression ($\overline{C}$ vs Cref). As a criterion of linearity, the maximum accepted value as residual is 5%.

2.3.3 Repeatability, reproducibility and robustness of the method

The repeatability and reproducibility derived from the inter-laboratory comparison exercise results were calculated after the elimination of outliers identified by Mandel's h and k statistic:

The ***inter-laboratory consistency*** is determined by the statistic h, which represents the ratio between the bias of the measure with respect to the average value, $\overline{C_i}$, and the standard deviation of the average inter-laboratory values, $S_{\overline{C_i}}$.

The ***intra-laboratory consistency*** is determined by the statistic k, which is defined by the ratio between the laboratory standard deviation of the sample, si, and the pooled within-laboratory standard deviations:

$$k_i = \frac{s_i}{\sqrt{\frac{\sum s_i^2}{p}}}$$

Eq. 4

Indicators for Mandel's statistics at the 1 and 5 % level of significance are given in the annex: Indicators of Mandel's statistics. These values determine the outliers and stragglers, respectively.

As a result, the uncertainty of the inter-laboratory average value, $\overline{\overline{C}}$, is determined by the combination of the inter-laboratory variance, s_L^2, and the intra-laboratory variance (repeatability variance), s_r^2. The addition of both variances represents the reproducibility variance, s_R^2, in this case being the variance associated with the uncertainty of the method [ISO 5725 Part 1, Part 2, 1994]:

$$u = \sqrt{s_L^2 + s_r^2} = s_R$$

Eq. 5

being

$$s_r^2 = \frac{1}{p}\sum_i^p s_i^2$$

$$s_R^2 = \frac{1}{p-1}\sum_i^p \left(\overline{C}_i - \overline{\overline{C}}\right)^2 + \left(1 - \frac{1}{n}\right)\cdot s_r^2$$

Eq. 6, Eq. 7

where 'p' is the number of laboratories; 'n' is the number of replicated analyses done by each laboratory; 'si' and '$\overline{C_i}$' are the standard deviation and average value corresponding to the laboratory 'i'.

The null hypothesis for equivalence between the inter-laboratory averages can be used as a criterion for the robustness of the method tested. Such an hypothesis assumes a F-distribution with p-1 and p(n-1) degrees of freedom for the statistic F defined by the ratio: s_L^2 / s_r^2 This unilateral test for the F-distribution statistic depends on the degrees of freedom (experimental design: number of participating laboratories and replicated samples) and the accepted significance level. As a conservative approach, methods with F-values lower than 3 can be considered as robust methods. This criterion expressed as a ratio between reproducibility and

repeatability standard deviations implies gamma values, γ, lower than 2, being γ = sR/sr [P. Pérez Ballesta et al., 2001].

2.3.4 Repeatability score

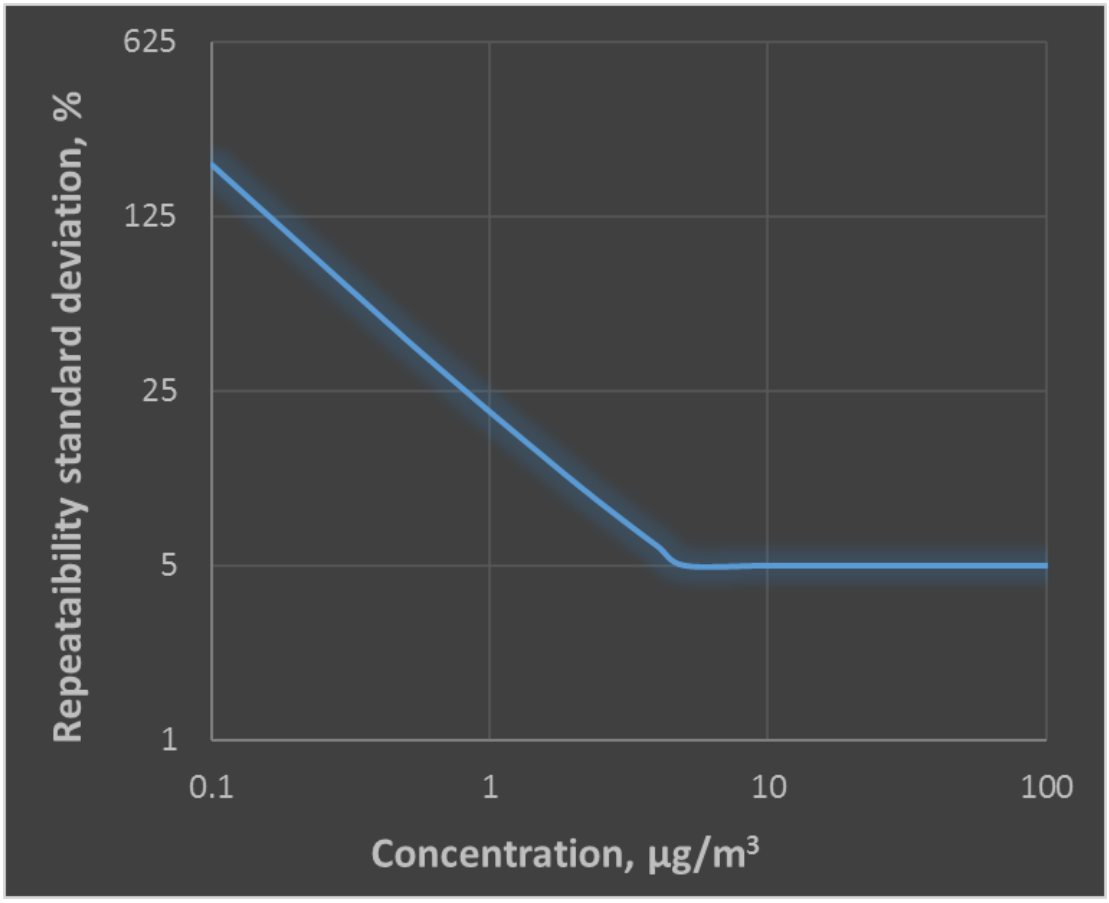
Following the AQUILA N37 recommendations, the standard deviation for the proficiency assessment, σN37, is calculated as a function of the concentration level in µg/m3, C, by the following equation:

$$\hat{\sigma}_{N37} = 0.128 + 0.057 \cdot C$$

Eq. 8

To evaluate the performance criterion as established by EN 14662-3 for benzene automatic analysers, a repeatability score has been derived from the k-statistic. Therefore, from a minimum value of repeatability standard deviation of 5 %, at concentrations over the limit value (i.e. 0.25 µg/m3), until 0.2 µg/m3 for values lower than 0.1 x LV by considering a linear decrease of the absolute value of the standard deviation in between was considered (see Figure 1). Therefore, the pooled-within-laboratory standard deviation is replaced by the corresponding maximum accepted repeatability value or, alternatively by the associated uncertainty of the reference value, when this value is limiting the repeatability test. Repeatability scores values lower than $\sqrt{2}$ are considered acceptable, between $\sqrt{2}$ and $\sqrt{3}$ are questionable and higher than $\sqrt{3}$, i.e. outside the 99 % confidence level, are considered as poor performers.

Figure 1. Repeatability standard deviation: Performance criteria according to EN 14662-3



2.3.5 Minimum standard deviation of the proficiency assessment

In agreement with ISO 13528, the ratio between the between-laboratory standard deviation of the inter-laboratory comparison, s_L, and that derived from the prescribed standard deviation for the proficiency assessment, sLN37, should be lower than 2 to represent a realistic choice. Therefore, as the inter-laboratory standard deviation from the prescribed conditions of proficiency assessment is calculated according to the following expression:

$$s_{L_{N37}} = \sqrt{\hat{\sigma}^2_{N37} - \frac{s_r^2}{n}}$$

Eq. 9

the minimum standard deviation of proficiency assessment coherent with method reproducibility, $\hat{\sigma}_m$, can be calculated by the following equation (ISO 13528):

$$\hat{\sigma}_m = \sqrt{(0.5 \cdot s_L)^2 + \frac{s_r^2}{n}}$$

Eq. 10

Therefore, when $\hat{\sigma}_{N37}$ is higher than $\hat{\sigma}_M$ the AQUILA N37 proposed value for the standard deviation for proficiency assessment is coherent with the reproducibility of the measurements. Otherwise, the corresponding expected reproducibility standard deviations cannot be achieved in practice.

2.3.6 E_n values

As laboratories were requested to report uncertainty values for each concentration level, the evaluation of the laboratory performance was based on the E_n number as recommended by ISO/EC Guide 43-1:1997, A.2.1.4 item E. This number is calculated according to the following equation:

$$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U^2_{lab} + U^2_{ref}}}$$

Eq. 11

where U_{lab} and U_{ref} are the expanded uncertainties for the laboratory and reference value respectively. E_n number evaluates the compatibility between bias and expanded uncertainty for each result. The critical value for E_n number is 1. E_n numbers higher than 1 identify results that are incompatible with the reference value after allowing for the stated uncertainties. The overall evaluation of the laboratory results should consider both bias and E_n value because a low En value could be due to a large stated uncertainty.

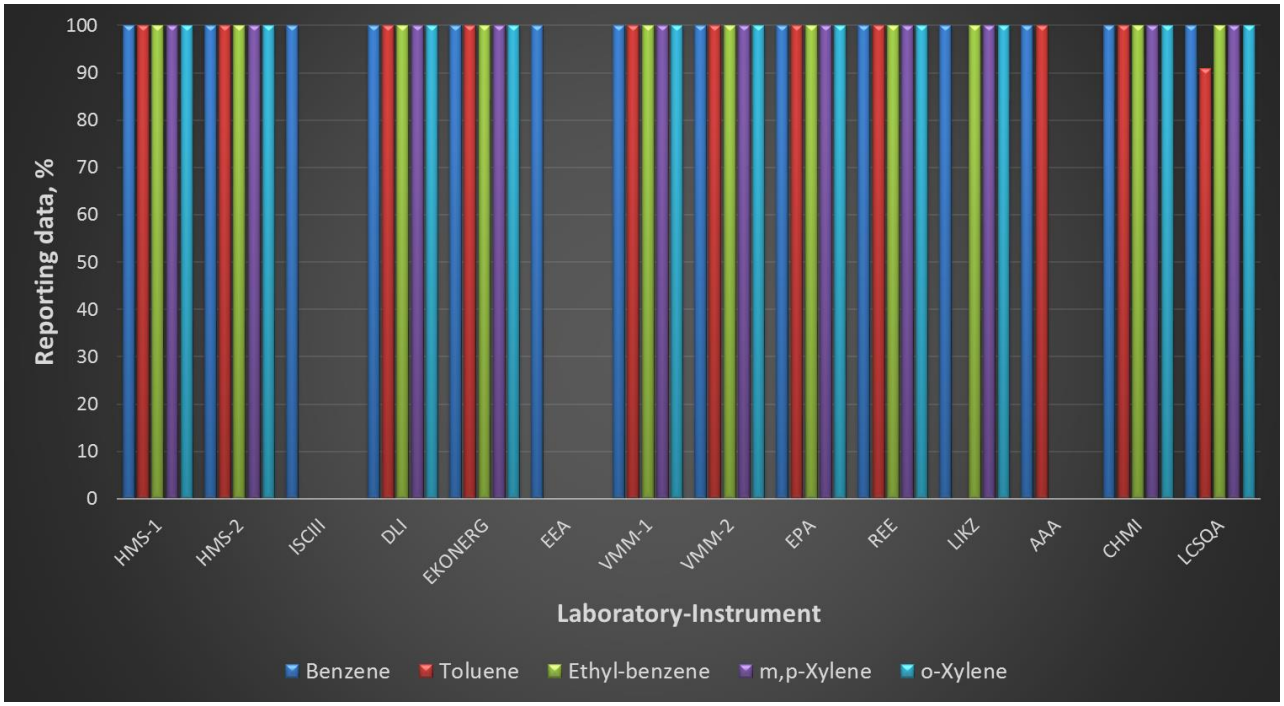
3 RESULTS AND DISCUSSION

3.1 Data reporting

Figure 2 represents for each participant, instrument and compound, the percentage of reported data in the up and down series of concentrations with respect to the total data set.

Although this was not a common trend, some laboratories limited the number of reported compounds: ISCIII and EEA reported only benzene, while AAA reported only benzene and toluene. LIKZ did not report toluene and LCSQA did not report the highest level of toluene concentration. EPA did not provide uncertainties for the C8 aromatic compounds.

Figure 2. Percentage of data compounds reported by the participating laboratories and instruments



3.2 Linearity test

Table 5 to Table 7 show the results of the linearity test for the correlation between reported and reference values. Residuals were calculated by Eq.3. In these tables, the percentage of residuals was indicated for those values higher than 5 %. Values were highlighted in red when these were higher than 10 %. Linearity problems were frequently identified at the lowest concentration levels, eventually with higher incidence on the heaviest compounds and with slightly higher frequency in those instruments using Tenax GR. The use or not of multi-calibration points seems to be critical for the linearity of the response. Therefore, by comparing multi-calibration points with respect to one point calibration, it is observed that most of the underestimations were related to the one point calibration procedure.

Table 5. Linearity tests for benzene and toluene

BENZENE	HMS-1	HMS-2	ISCIII	DLI	EKONERG	EEA	VMM-1	VMM-2	EPA	REE	LIKZ	AAA	CHMI	LCSQA
1st -A	6	OK	13	-18	OK	-38	-78	15	-24	-8	OK	-68	-6	15
2nd -A	OK	OK	-5	OK	OK	-10	-24	OK	-6	OK	OK	-23	OK	OK
3rd -A	OK	OK	-6	OK	OK	12	OK	OK	OK	OK	OK	-15	OK	OK
4th -A	OK	OK	OK	OK	OK	OK	8	OK	7	OK	OK	23	OK	OK
5th -A	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	9	OK	OK
6th	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	-6	OK	OK
5th -B	OK	OK	OK	OK	OK	OK	6	OK	OK	OK	OK	5	OK	OK
4th -B	OK	OK	OK	OK	OK	OK	15	OK	OK	OK	OK	15	OK	OK
3rd -B	OK	OK	OK	OK	OK	11	OK	OK	OK	OK	OK	-16	OK	OK
2nd -B	OK	OK	OK	OK	OK	-9	-13	OK	OK	OK	OK	-25	-6	OK
1st -B	6	OK	12	-8	OK	-44	-62	15	-18	OK	OK	-74	-13	OK

TOLUENE	HMS-1	HMS-2	ISCIII	DLI	EKONERG	EEA	VMM-1	VMM-2	EPA	REE	LIKZ	AAA	CHMI	LCSQA
1st -A	7	OK		-11	OK		-21	-7	-5	OK		-23	-5	OK
2nd -A	OK	OK		-8	-6		OK	OK	8	OK		-7	-7	OK
3rd -A	OK	OK		-11	OK		OK	OK	9	OK		OK	-6	OK
4th -A	OK	OK		-12	OK		-8	OK	OK	OK		OK	OK	OK
5th -A	7	OK		-11	OK		-27	OK	OK	OK		OK	OK	5
6th	-15	OK		-12	-6		-29	OK	-8	OK		OK	OK	
5th -B	7	OK		-8	OK		-24	OK	-6	OK		-7	OK	5
4th -B	OK	OK		-8	-6		OK	OK	OK	OK		OK	OK	OK
3rd -B	OK	OK		-7	-7		12	OK	OK	OK		-6	-6	OK
2nd -B	OK	OK		OK	-8		18	-5	9	OK		OK	-5	OK
1st -B	OK	-7		OK	-10		13	-5	OK	OK		-31	OK	-12

Table 6. Linearity test for ethyl-benzene and m,p-xylene

ETHYLBENZENE	HMS-1	HMS-2	ISCIII	DLI	EKONERG	EEA	VMM-1	VMM-2	EPA	REE	LIKZ	AAA	CHMI	LCSQA
1st -A	**13**	7		**-26**	7		**-63**	**55**	**-54**	-6	**OK**		**-14**	**15**
2nd -A	**OK**	**OK**		**-18**	**-10**		**-32**	7	**-23**	-9	**OK**		-9	**OK**
3rd -A	**OK**	**OK**		-6	**OK**		**-17**	-7	**OK**	-6	5		-7	**OK**
4th -A	**OK**	6		6	**OK**		**OK**	**-12**	9	**OK**	**OK**		**OK**	**OK**
5th -A	**OK**	**OK**		**OK**	**OK**		**OK**	**OK**	**OK**	**OK**	**OK**		**OK**	**OK**
6th	**OK**	**OK**		**OK**	**OK**		**OK**	**OK**	**OK**	**OK**	**OK**		**OK**	**OK**
5th -B	**OK**	**OK**		**OK**	**OK**		6	**OK**	**OK**	**OK**	**OK**		**OK**	**OK**
4th -B	**OK**	**OK**		9	**OK**		**19**	**-12**	7	**OK**	**OK**		**OK**	**OK**
3rd -B	**OK**	**OK**		**OK**	**OK**		9	**OK**	**OK**	**OK**	**OK**		**OK**	**OK**
2nd -B	**OK**	-5		-9	**OK**		-9	**15**	**-12**	**OK**	**OK**		**OK**	**OK**
1st -B	**12**	**OK**		**-22**	7		**-43**	**64**	**-38**	6	**OK**		10	10

MP-XYLENE	HMS-1	HMS-2	ISCIII	DLI	EKONERG	EEA	VMM-1	VMM-2	EPA	REE	LIKZ	AAA	CHMI	LCSQA
1st -A	**21**	**18**		**-50**	5		9	**74**	**-67**	**-24**	**-17**		**-18**	**51**
2nd -A	**OK**	6		**-28**	**-15**		**-28**	**17**	**-29**	**-13**	**OK**		**-13**	**OK**
3rd -A	**OK**	-6		-9	**OK**		**-20**	-5	-6	-6	9		-9	**OK**
4th -A	**OK**	**OK**		9	**OK**		-6	**-19**	**13**	**OK**	7		**OK**	**OK**
5th -A	**OK**	**OK**		**OK**	**OK**		**OK**	**OK**	7	**OK**	**OK**		**OK**	**OK**
6th	**OK**	**OK**		**OK**	**OK**		**OK**	**OK**	-6	**OK**	**OK**		**OK**	**OK**
5th -B	**OK**	**OK**		5	**OK**		6	**OK**	6	**OK**	**OK**		**OK**	**OK**
4th -B	**OK**	**OK**		**15**	**OK**		**14**	**-21**	**12**	8	**OK**		**OK**	-7
3rd -B	**OK**	-9		**OK**	**OK**		7	**OK**	**OK**	**OK**	**OK**		**OK**	**OK**
2nd -B	**OK**	**OK**		**-16**	**OK**		**OK**	**18**	**-18**	**OK**	-6		**OK**	**OK**
1st -B	**11**	8		**-44**	**OK**		**-22**	**72**	**-53**	**-22**	**-41**		**OK**	**33**

Table 7. Linearity test for o-xylene

O-XYLENE	HMS-1	HMS-2	ISCIII	DLI	EKONERG	EEA	VMM-1	VMM-2	EPA	REE	LIKZ	AAA	CHMI	LCSQA
1st -A	**14**	**10**		**-16**	9		**-123**	**10**	**-144**	**-19**	**22**		**-12**	**43**
2nd -A	**OK**	**OK**		**-18**	-6		**-32**	**OK**	**-30**	**-12**	**OK**		**-12**	**10**
3rd -A	**OK**	**OK**		-7	**OK**		**-12**	**OK**	8	-5	**OK**		**-11**	**OK**
4th -A	**OK**	**OK**		10	**OK**		**OK**	**OK**	**22**	**OK**	**OK**		-6	**OK**
5th -A	**OK**	**OK**		**OK**	**OK**		**OK**	**OK**	**OK**	**OK**	**OK**		**OK**	**OK**
6th	**OK**	**OK**		**OK**	**OK**		**OK**	**OK**	**OK**	**OK**	**OK**		**OK**	**OK**
5th -B	**OK**	**OK**		**OK**	**OK**		8	**OK**	**OK**	**OK**	**OK**		6	**OK**
4th -B	**OK**	**OK**		**15**	**OK**		**21**	**OK**	**19**	7	**OK**		6	**OK**
3rd -B	**OK**	-6		**OK**	**OK**		**11**	**OK**	10	**OK**	**OK**		**OK**	**OK**
2nd -B	**OK**	-6		**-14**	**OK**		-7	**OK**	**-15**	**OK**	-7		**OK**	5
1st -B	**OK**	-6		-17	**OK**		-7	OK	-14	**OK**	-9		6	**OK**

3.3 Comparison between reference and robust average value

Assigned values acting as reference can be compared to the robust average derived from the result of each concentration level. The robust average value, $\overline{C_i}^*$, and its standard deviation, s*, is calculated according to ISO 13528 (see annex: Robust Analysis).

Assuming a normal distribution for the bias, $\overline{C_i}^* - C_{ref}$, the associated standard uncertainty is estimated as:

$$s_{bias} = \sqrt{\frac{(1.25 \cdot s^*)^2}{p} + u_{C_{ref}}^2}$$

Eq. 12

where p is the number of participating laboratories.

The null hypothesis for a bias equal to zero can be evaluated using the two tails statistical test of normal distribution of the random variable, Z, defined as:

$$Z = \frac{\overline{C_i}^* - C_{ref}}{s_{bias}}$$

Eq. 13

For which the probability function of the distribution for a confidence level of (1-α) is:

$$P(-Z_{1-\alpha/2} < Z < Z_{1-\alpha/2}) = 1 - \alpha$$

Eq. 14

α represents the level of significance of the test. P values lower than 0.95 imply no significant bias and the bias becomes significant with the increase of the P value.Table **8** shows the results of the statistical test. Significant biases with α values lower than 0.01 could occasionally be observed for lower concentration levels for the heaviest aromatic compounds, C8, when compared with the robust average of all the participant (α_1, $Bias_1$). However, such observations disappeared when results from instrument using Tenax GR were excluded (α_2, $Bias_2$).

In general, the higher analytical uncertainties assigned to low concentrations were covering the increasing bias at these concentration levels. It is however noted a trend to under-estimate the lower concentrations in particular for C8 aromatic compounds and those instruments that used one-point-calibration point strategy.

Altogether, this test ensures the reference values and associated uncertainties as being coherent with the robust average values of the inter-laboratory comparison.

Table 8. Robust average value, level of significance and bias with respect to the reference value

Level	Benzene	α_1	α_2	$Bias_1$, %	$Bias_2$, %	Toluene	α_1	α_2	$Bias_1$, %	$Bias_2$, %
1ST-A	1.44	0.144	0.354	-9.02	-6.36	3.27	0.406	0.973	-5.17	0.22
2ND-A	3.02	0.256	0.928	-3.88	-0.48	10.92	0.365	0.997	-2.46	0.01
3RD-A	5.29	0.571	0.917	-1.39	0.44	19.52	0.670	0.937	-0.86	0.18
4TH-A	10.38	0.864	0.538	0.45	3.98	39.09	0.381	0.702	-3.00	-1.61
5TH-A	31.37	0.775	0.840	-0.64	0.66	118.56	0.333	0.470	-4.20	-3.87
6TH-A	52.31	0.271	0.257	-2.29	-2.28	190.57	0.063	0.151	-10.73	-8.25
5TH-B	31.32	0.947	0.764	-0.16	0.97	119.24	0.317	0.440	-4.17	-3.95
4TH-B	10.62	0.867	0.587	-0.47	4.16	40.57	0.150	0.503	-3.79	-1.09
3RD-B	5.38	0.518	0.985	-1.62	0.09	20.33	0.396	0.895	-2.35	0.59
2ND-B	3.10	0.194	0.893	-3.49	-0.79	11.58	0.388	0.957	-2.47	0.28
1ST-B	1.49	0.036*	0.266	-9.56	-6.25	3.84	0.158	0.633	-6.44	-2.60
Level	Ethyl-benzene	α_1	α_2	$Bias_1$, %	$Bias_2$, %	mp-Xylene	α_1	α_2	$Bias_1$, %	$Bias_2$, %
1ST-A	0.87	0.019*	0.219	-29.55	-15.67	1.08	0.065	0.605	-29.56	-8.69
2ND-A	2.18	0.001▪	0.044	-19.92	-10.93	2.41	0.003▪	0.073	-21.35	-12.56
3RD-A	3.79	0.008▪	0.124	-11.30	-7.35	4.17	0.012*	0.084	-11.79	-9.45
4TH-A	7.30	0.331	0.951	-3.92	0.28	7.91	0.555	0.769	-2.33	-1.24
5TH-A	21.80	0.360	0.528	-3.16	1.69	23.71	0.866	0.937	-0.58	0.30
6TH-A	35.26	0.172	0.764	-4.90	-1.31	38.37	0.493	0.811	-2.72	-1.04
5TH-B	22.09	0.451	0.494	-2.56	2.28	24.18	0.975	0.544	-0.10	1.92
4TH-B	7.71	0.392	0.678	-3.86	2.81	8.49	0.793	0.700	-1.04	2.02
3RTD-B	3.92	0.077	0.919	-7.42	-0.60	4.36	0.104	0.708	-7.00	-2.18
2ND-B	2.28	0.030*	0.637	-12.02	-2.60	2.61	0.034*	0.545	-13.92	-3.89
1ST-B	0.95	0.015*	0.382	-22.04	-6.81	1.18	0.019*	0.291	-31.10	-12.07
Level	o-Xylene	α_1	α_2	$Bias_1$, %	$Bias_2$, %					
1ST-A	0.88	0.072	0.162	-27.02	-24.03					
2ND-A	2.32	0.004▪	0.048*	-16.31	-13.00					
3RD-A	4.11	0.019*	0.090	-9.82	-7.61					
4TH-A	7.98	0.326	0.655	-3.46	-1.55					
5TH-A	23.84	0.182	0.871	-3.95	-0.37					
6TH-A	38.78	0.106	0.328	-4.73	-3.37					
5TH-B	24.12	0.381	0.717	-2.48	1.16					
4TH-B	8.44	0.894	0.686	-0.64	2.64					
3RD-B	4.35	0.300	0.881	-5.70	-0.91					
2ND-B	2.52	0.072	0.326	-11.52	-4.99					
1ST-B	1.04	0.021*	0.232	-22.33	-10.07					

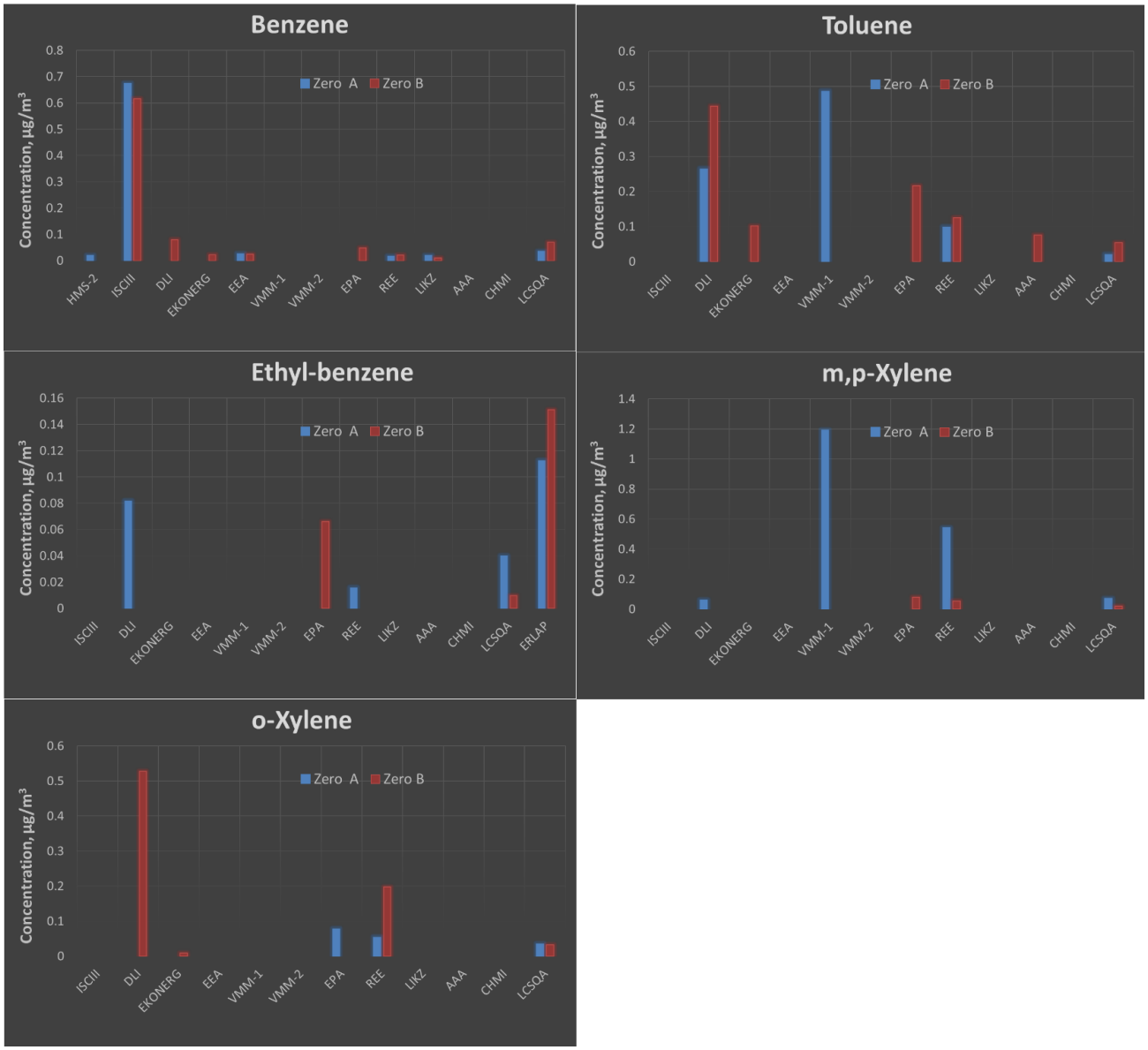
*: 95-99 % confidence level, (1- α) ▪ : > 99% confidence level, (1- α),

$Bias_1$, α_1: Bias and Probability with respect to all samples, $Bias_2$, α_2: Probability with respect to temperature desorbed samples

3.4 Blank levels

Figure 3 shows the concentrations reported by the participants during the zero air concentration steps (Zero-A and Zero-B). As median of the measured values, depending on the compound and the instrument, these blank values represented between 5 and 21 % of the concentration at the 1st step level and they were in the same range of the corresponding expanded uncertainties at that step.

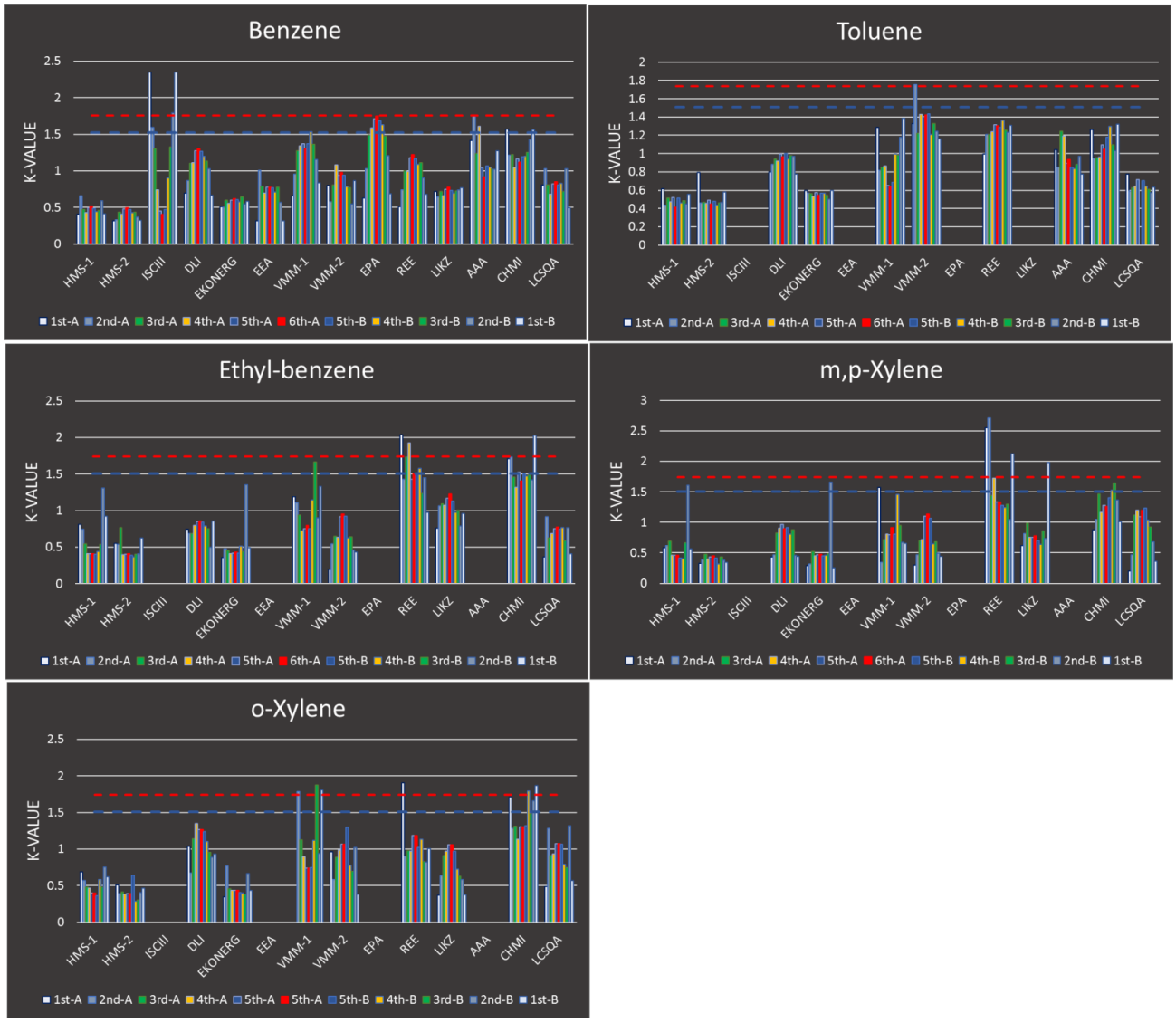
Figure 3. Reported blank levels



3.5 Outliers, repeatability, reproducibility and robustness of the method

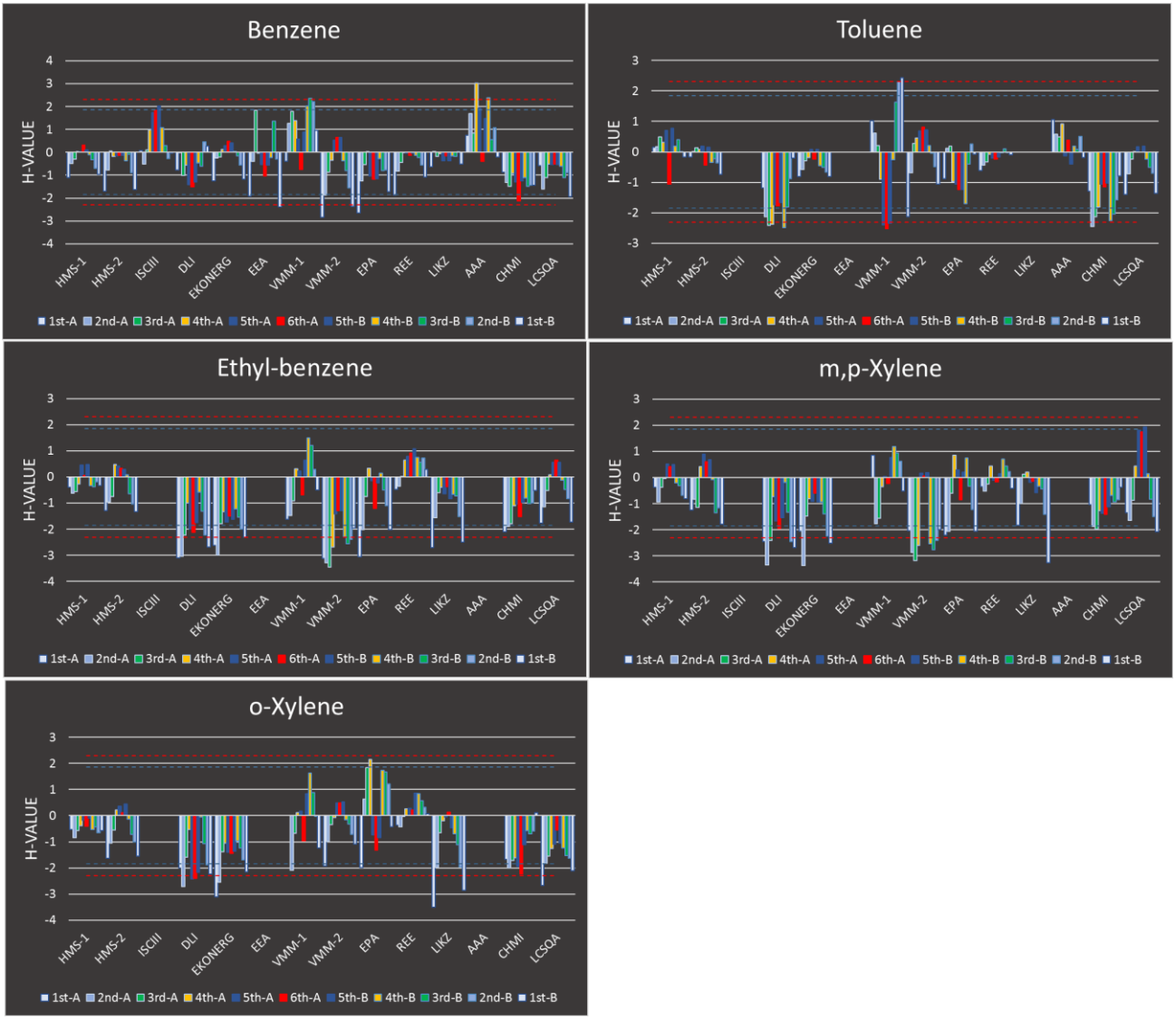
As indicated in the previous section, repeatability and reproducibility standard deviation were calculated after elimination of the outliers identified by the k and h statistics. The results of these statistics are shown in Figure 4 and Figure 5**,** respectively. The values of repeatability, reproducibility standard deviation are represented in Figure 6, while Figure 7 shows the corresponding robustness derived for each concentration level and compound.

Figure 4. k-values for the reported concentrations of the comparison exercise



------ and ------- correspond to the 99 and 95 % confidence level)

Figure 5. h-values for the reported concentrations of the comparison exercise



-------- h1: 99 % confidence level: outlier identification --------- h2: 95 % confidence level: straggler identification

*K Values of EPA for toluene, ethyl-benzene and xylenes were excluded as uncertainty values were not provided for these compounds

Figure 6. Repeatability and reproducibility of the inter-laboratory exercise

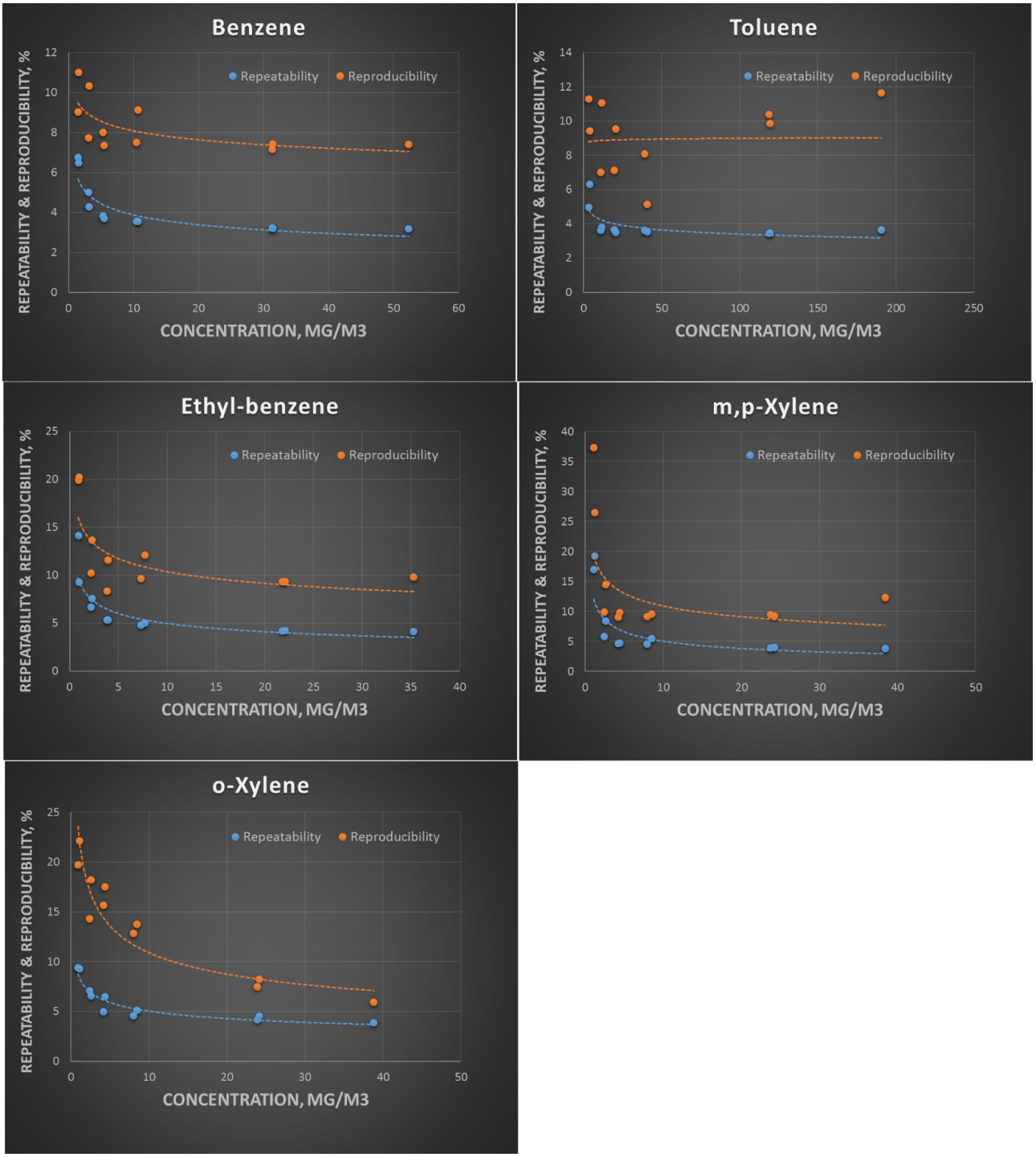
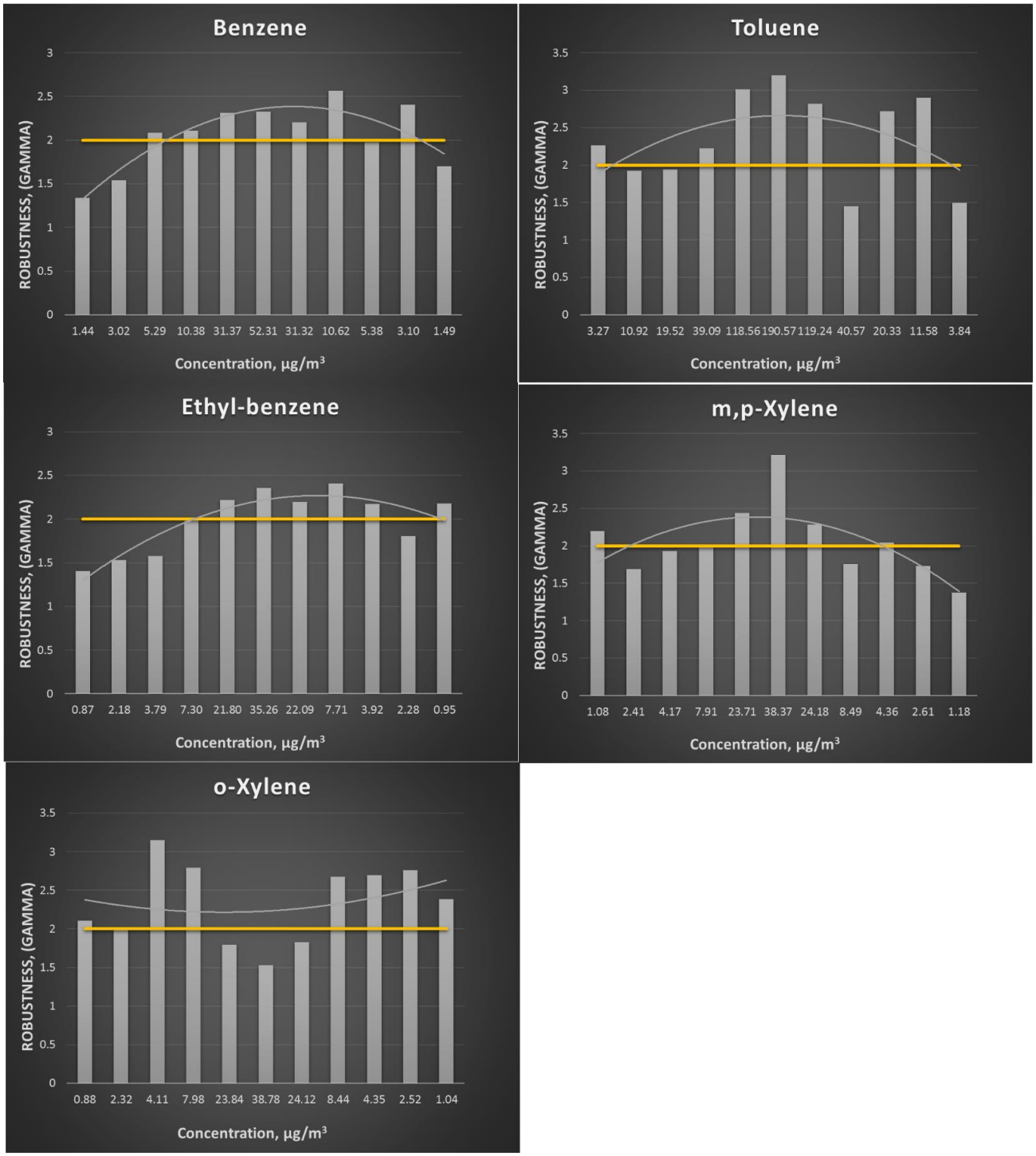


Figure 7. Robustness of the inter-laboratory exercise



As expected, Figure 6 shows that the values of repeatability and reproducibility increased with the decrease in the concentration. As already observed for toluene in previous exercise, the increase of its reproducibility value at higher concentrations was associated with the lack of linearity due to breakthrough problems for some of the instruments.

In comparison with the previous inter-laboratory comparison (EUR 27012EN), a general improvement of the reproducibility and repeatability values and in particular the C8 aromatic compounds is noted. This observation is also consistent with the average gamma values and the improved method's robustness (Table 9).

Table 9. Average repeatability, reproducibility and γ values of the inter-laboratory exercise

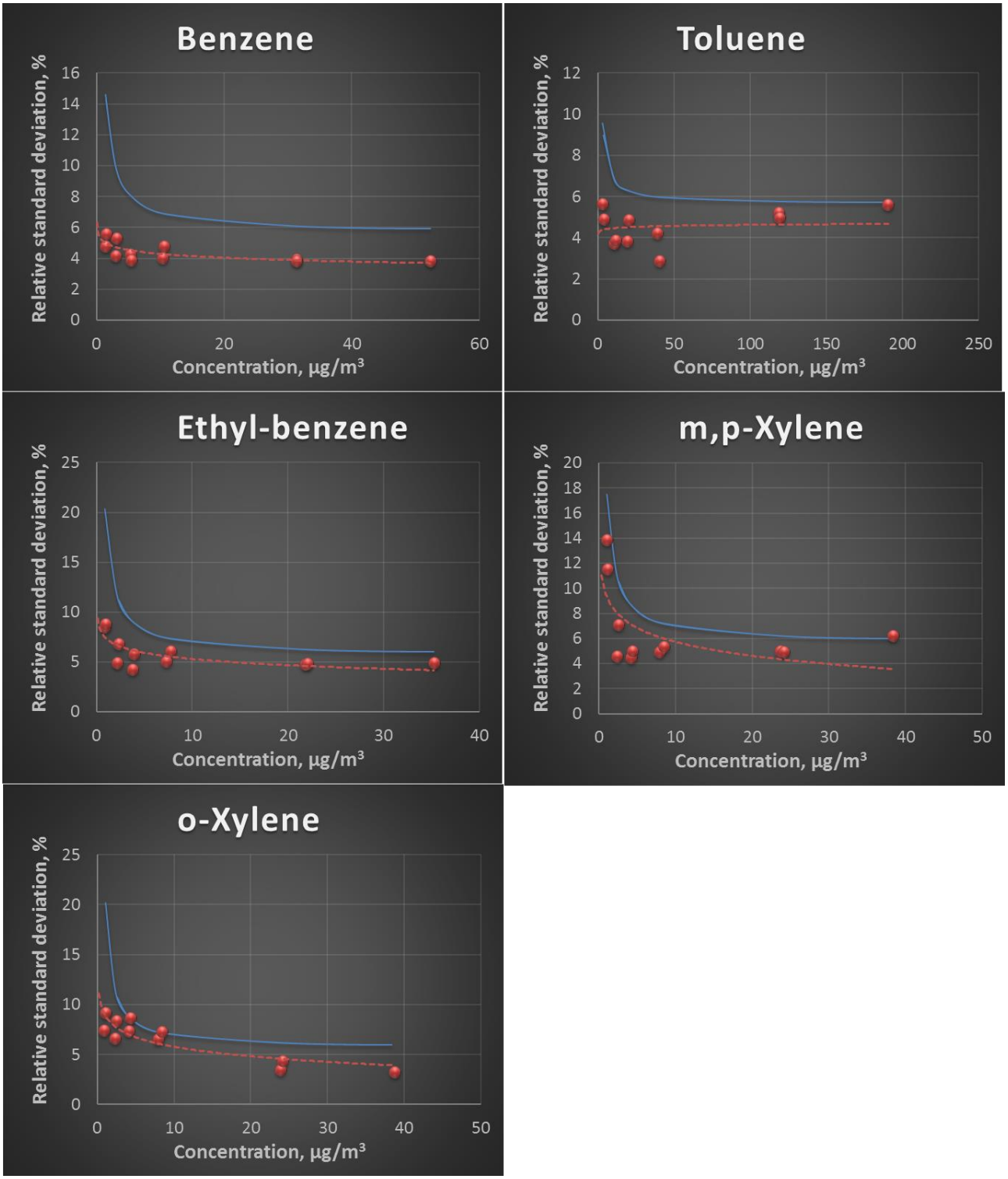
	Repeatability, %	**Reproducibility, %**	**Robustness (γ)**
Benzene	4.26	8.38	2.05
Toluene	3.97	9.15	2.36
Ethyl-benzene	6.44	12.22	1.99
m,p-Xylene	7.46	14.31	2.06
o-Xylene	6.02	14.19	2.34

Exercises results without outliers. Repeatability, reproducibility and robustness values of previous inter-laboratory exercises are provided in the annex: Average repeatability, reproducibility and gamma values of 2nd and 3rd inter-laboratory exercise

3.6 Standard deviation of the proficiency assessment N37

An overall evaluation of the method can be obtained from the comparison of the minimum acceptable standard deviation compatible with the reproducibility of the exercise and the standard deviation for proficiency assessment N37. In Figure 8 both relative standard deviations are represented for the compounds compared and their concentration ranges. For the estimation of the corresponding reproducibility values and standard deviation, outliers identified with the k and h test were excluded. As shown in the Figure 8, the minimum relative standard deviations calculated from the proficiency test, excluding outliers, complied with the N37 criteria for all compounds and concentrations.

Figure 8. Minimum standard deviation compatible with reproducibility of the tests and standard deviation for proficiency assessment N37



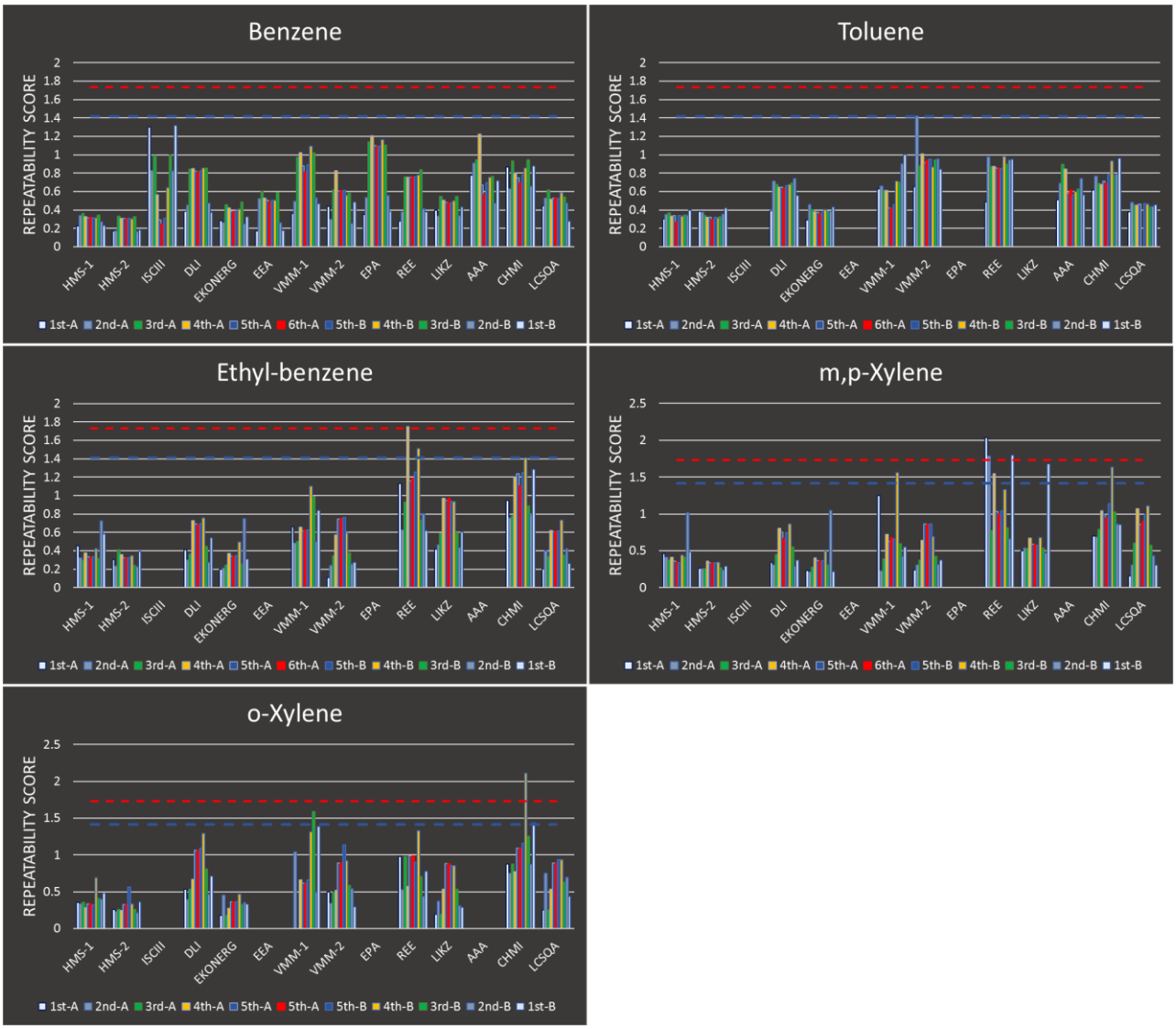
_____ Relative standard deviation from AQUILA N37 proposal, $\hat{\sigma}_{N37}$/Cref .100

--O-- Minimum relative standard deviation compatible with the reproducibility of the exercise, $\hat{\sigma}_{m}$/Cref .100

3.7 Repeatability-score and E_n value

The individual evaluation of the laboratory test performance was carried out by means of the previously defined repeatability-score and E_n value. Results from the repeatability score are shown in Figure 9. Repeatability values over the red line correspond to reported uncertainties that exceed the criteria considered by the N37 and EN 14662-3.

Figure 9. Repeatability-score (N37) for the inter-laboratory comparison exercise



-------- 99 % confidence level: outlier identification --------- 95 % confidence level: straggler identification

Repeatability score of EPA for toluene, ethyl-benzene and xylenes were excluded as uncertainty values were not provided for these compounds.

E_n values were determined for each instrument and reported concentration. The results are shown in Table 10 to Table 14. In these tables, under the "state" column, the E_n values that did not fulfil the test criteria are highlighted in orange as a "warning" (E_n> 1) or in red as a "action" (if E_n> 1.5). The U % values with repeatability score over the limit criteria (99 % confidence level) are also highlighted in red.

Repeatability score and E_n value can be considered as complementary tests in the evaluation of the results. As a relatively high reported uncertainty could compensate a high bias and, consequently, pass the E_n value test, the repeatability score test can, in such cases, identify this problem. In this exercise, this was the case for REE for ethyl-benzene at the 4th-A level (Table 12), m,p-xylene at the 1st-A, 2nd-A and 1st –B level (Table 13) and for CHMI for o-xylene at the 4th-B level (Table 14). In the case of the EPA, their E_n values and U % for toluene, ethyl-benzene and xylenes were not calculated as their uncertainties were not provided by the laboratory.

This statistical analysis provides an overview of the instrument performance for each participant. The interpretation and actions to be addressed as a consequence of the results are the responsibility of each laboratory and are outside the consideration of this report.

Table 10. E_n value, bias and reported expanded uncertainty of the participants: benzene

COMPOUND	HMS-1					HMS-2					ISCIII				
Benzene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	1.30	OK	-0.8	-9.5	6.5	1.23	warning	-1.3	-14.6	5.4	1.45	OK	0.0	0.7	34.2
2nd-A	2.91	OK	-0.4	-3.8	7.2	2.84	OK	-1.0	-6.0	3.7	2.90	OK	-0.2	-4.0	17.4
3rd-A	5.17	OK	-0.5	-2.3	3.7	5.31	OK	0.1	0.5	3.3	5.33	OK	0.1	0.8	9.9
4th-A	10.39	OK	0.0	0.1	3.3	10.17	OK	-0.5	-1.9	3.2	11.53	Action	1.8	11.1	5.1
5th-A	31.39	OK	0.0	0.0	3.2	31.05	OK	-0.3	-1.0	3.1	35.17	Action	3.8	12.1	2.6
6th-A	53.43	OK	0.6	2.2	3.2	51.83	OK	-0.3	-0.9	3.1	58.84	Action	4.4	12.5	2.2
5th-B	31.53	OK	0.2	0.7	3.1	31.02	OK	-0.3	-1.0	3.1	35.53	Action	3.7	13.4	2.7
4th-B	10.48	OK	-0.3	-1.3	3.2	10.19	warning	-1.0	-4.0	3.2	11.87	Action	1.7	11.8	5.8
3rd-B	5.23	OK	-0.7	-2.8	3.5	5.34	OK	-0.2	-0.7	3.3	5.52	OK	0.2	2.5	9.7
2nd-B	2.90	warning	-1.1	-6.4	5.8	2.85	Action	-2.0	-8.0	3.6	3.03	OK	-0.2	-2.5	16.9
1st-B	1.34	warning	-1.1	-9.5	6.5	1.25	Action	-2.1	-16.1	5.5	1.48	OK	0.0	-0.3	33.7
	DLI					EKONERG					EEA				
Benzene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	1.34	OK	-0.5	-6.7	11.0	1.28	OK	-0.8	-10.6	8.4	1.20	warning	-1.4	-16.49	5.5
2nd-A	3.02	OK	0.0	-0.1	9.1	2.96	OK	-0.3	-2.0	5.3	2.93	OK	-0.3	-3.09	10.8
3rd-A	4.90	OK	-0.8	-7.4	9.1	5.21	OK	-0.3	-1.5	4.6	6.00	Action	2.1	13.43	5.3
4th-A	9.70	OK	-0.7	-6.5	9.1	10.54	OK	0.3	1.5	4.2	10.32	OK	-0.1	-0.58	5.3
5th-A	28.26	warning	-1.2	-9.9	9.1	31.99	OK	0.5	2.0	3.8	30.18	OK	-0.7	-3.81	5.2
6th-A	46.90	warning	-1.3	-10.3	9.0	54.04	OK	0.8	3.3	3.7	48.60	warning	-1.4	-7.08	5.2
5th-B	28.62	warning	-1.0	-8.6	9.0	32.20	OK	0.6	2.8	3.8	30.15	OK	-0.7	-3.74	5.2
4th-B	10.08	OK	-0.6	-5.1	9.0	10.65	OK	0.1	0.3	4.1	10.34	OK	-0.5	-2.63	5.2
3rd-B	5.10	OK	-0.6	-5.3	9.0	5.31	OK	-0.3	-1.4	4.9	6.03	Action	1.9	11.98	5.2
2nd-B	3.23	OK	0.4	4.2	9.1	2.95	OK	-0.9	-5.0	5.3	3.02	OK	-0.5	-2.84	5.4
1st-B	1.52	OK	0.2	2.6	9.3	1.31	warning	-1.1	-11.6	9.5	1.14	Action	-3.2	-23.49	5.9
	VMM-1					VMM-2					EPA				
Benzene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	1.39	OK	-0.2	-3.42	10.0	1.09	Action	-1.5	-24.32	15.5	1.11	Action	-1.6	-22.67	12.0
2nd-A	3.32	OK	0.9	9.66	9.1	2.59	Action	-1.8	-14.35	7.0	2.74	OK	-0.8	-9.52	11.9
3rd-A	5.98	warning	1.3	13.05	8.6	4.95	OK	-1.0	-6.40	6.6	5.08	OK	-0.3	-3.96	11.8
4th-A	12.00	Action	1.5	15.69	8.8	9.98	OK	-0.5	-3.84	8.6	10.40	OK	0.0	0.23	12.0
5th-A	32.62	OK	0.4	3.97	8.5	32.51	OK	0.6	3.63	5.8	29.10	OK	-0.7	-7.25	11.8
6th-A	49.64	OK	-0.6	-5.10	8.6	54.58	OK	0.7	4.34	5.8	48.09	OK	-0.7	-8.05	11.8
5th-B	33.15	OK	0.6	5.84	8.4	32.66	OK	0.7	4.29	5.9	28.89	OK	-0.7	-7.75	11.8
4th-B	12.96	Action	2.0	22.04	8.9	10.17	OK	-0.7	-4.18	5.8	10.30	OK	-0.2	-2.96	12.0
3rd-B	6.50	Action	2.0	20.79	8.5	5.01	warning	-1.1	-6.99	6.2	5.00	OK	-0.6	-7.09	11.9
2nd-B	3.73	Action	1.8	20.08	8.8	2.67	Action	-2.5	-14.13	5.8	2.89	OK	-0.6	-6.98	11.9
1st-B	1.63	OK	0.7	9.36	10.9	1.14	Action	-1.7	**-23.45**	16.2	1.24	warning	-1.5	-16.90	11.8
	REE					LIKZ					AAA				
Benzene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	1.21	warning	-0.2	-15.91	8.9	1.36	OK	-0.1	-5.40	11.2	1.53	OK	0.1	6.40	19.5
2nd-A	2.84	OK	-0.2	-6.21	8.2	3.03	OK	0.0	0.12	6.7	3.42	OK	0.4	13.03	16.2
3rd-A	5.12	OK	-0.2	-3.31	7.9	5.22	OK	-0.1	-1.35	5.5	5.61	OK	0.3	6.06	8.9
4th-A	10.37	OK	0.0	-0.02	7.6	10.29	OK	-0.1	-0.80	5.1	13.95	Action	3.6	34.47	9.1
5th-A	31.31	OK	-0.1	-0.20	7.6	30.57	OK	-0.8	-2.57	4.9	35.57	Action	4.2	13.39	5.9
6th-A	51.80	OK	-0.5	-0.98	7.7	51.78	OK	-0.5	-1.00	4.9	50.93	OK	-1.4	-2.64	5.9
5th-B	31.24	OK	-0.1	-0.25	7.6	30.54	OK	-0.8	-2.51	4.9	34.40	warning	3.1	9.84	6.3
4th-B	10.47	OK	-0.2	-1.42	7.9	10.43	OK	-0.2	-1.76	5.1	13.36	Action	2.7	25.81	6.0
3rd-B	5.27	OK	-0.1	-2.01	8.5	5.30	OK	-0.1	-1.55	5.6	5.64	OK	0.3	4.84	7.3
2nd-B	2.95	OK	-0.2	-5.07	8.8	3.11	OK	0.0	0.31	6.8	3.41	warning	0.3	9.78	8.6
1st-B	1.33	OK	-0.2	-10.78	10.9	1.41	OK	-0.1	-5.01	11.5	1.45	OK	0.0	-2.14	18.6
	CHMI					LCSQA									
Benzene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %					
1st-A	1.33	OK	-0.1	-7.46	24.9	1.36	OK	-0.1	-5.05	12.5					
2nd-A	2.72	OK	-0.3	-10.07	14.1	2.65	warning	-0.4	-12.23	12.2					
3rd-A	4.71	warning	-0.6	-10.91	10.5	4.86	warning	-0.4	-8.13	6.7					
4th-A	9.29	warning	-1.1	-10.45	8.9	9.78	warning	-0.6	-5.75	5.5					
5th-A	28.54	warning	-2.8	-9.04	8.2	30.19	OK	-1.2	-3.76	5.5					
6th-A	44.73	Action	-7.6	-14.49	8.2	50.51	OK	-1.8	-3.44	5.5					
5th-B	28.70	warning	-2.6	-8.38	8.5	30.20	OK	-1.1	-3.58	5.4					
4th-B	9.34	warning	-1.3	-12.06	9.7	9.91	warning	-0.7	-6.66	6.3					
3rd-B	4.67	warning	-0.7	-13.23	10.9	4.85	Action	-0.5	-9.88	6.0					
2nd-B	2.69	OK	-0.4	-13.18	15.1	2.85	OK	-0.3	-8.07	10.3					
1st-B	1.28	OK	-0.2	-14.10	26.0	1.20	Action	-0.3	-19.03	8.7					

Table 11. E_n value, bias and reported expanded uncertainty of the participants: toluene

COMPOUND		HMS-1					HMS-2					ISCIII				
Toluene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	3.32	OK	0.1	1.6	5.7	3.21	OK	-0.1	-1.7	7.6					
2nd-A	11.06	OK	0.3	1.2	3.5	10.93	OK	0.0	0.1	3.7					
3rd-A	20.32	warning	1.0	4.1	3.5	19.73	OK	0.3	1.1	3.3					
4th-A	40.23	OK	0.7	2.9	3.3	39.39	OK	0.2	0.8	3.2					
5th-A	128.80	Action	2.4	8.6	3.1	121.22	OK	0.6	2.2	3.1					
6th-A	164.95	Action	-4.1	-13.4	3.1	180.23	Action	-1.6	-5.4	3.1					
5th-B	129.49	Action	2.2	8.6	3.1	121.32	OK	0.5	1.7	3.1					
4th-B	41.09	OK	0.3	1.3	3.3	39.58	OK	-0.7	-2.4	3.2					
3rd-B	21.06	OK	1.0	3.6	3.3	19.94	OK	-0.5	-1.9	3.3					
2nd-B	11.59	OK	0.0	0.1	3.4	11.14	OK	-0.9	-3.8	3.7					
1st-B	3.74	OK	-0.3	-2.6	6.9	3.40	warning	-1.2	-11.6	7.9					
		DLI					EKONERG					EEA				
Toluene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	2.88	OK	-1.0	-11.8	8.5	3.01	OK	-0.7	-8.0	6.1					
2nd-A	9.21	Action	-2.0	-15.7	8.5	10.46	OK	-0.8	-4.3	4.8					
3rd-A	15.59	Action	-2.9	-20.1	8.5	19.04	OK	-0.6	-2.5	4.1					
4th-A	30.51	Action	-3.2	-22.0	8.3	38.40	OK	-0.4	-1.8	3.8					
5th-A	93.75	Action	-3.2	-20.9	8.2	119.78	OK	0.3	1.0	3.7					
6th-A	147.86	Action	-3.4	-22.4	8.2	184.79	OK	-0.8	-3.0	3.7					
5th-B	96.97	Action	-2.7	-18.7	8.2	120.43	OK	0.2	1.0	3.7					
4th-B	33.47	Action	-2.5	-17.5	8.2	39.27	OK	-0.7	-3.2	4.2					
3rd-B	17.06	Action	-2.3	-16.1	8.3	19.41	warning	-1.1	-4.5	4.0					
2nd-B	10.51	warning	-1.2	-9.2	8.2	10.77	Action	-1.5	-7.0	4.1					
1st-B	3.72	OK	-0.3	-3.3	9.7	3.36	warning	-1.3	-12.6	8.3					
		VMM-1					VMM-2					EPA				
Toluene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	3.60	OK	0.7	10.13	11.0	2.58	warning	-1.3	-21.11	15.9	2.98			-8.82	
2nd-A	11.43	OK	0.6	4.59	6.3	10.38	OK	-0.3	-4.99	14.9	11.02			0.91	
3rd-A	19.85	OK	0.3	1.71	6.0	19.97	OK	0.3	2.30	8.6	19.81			1.51	
4th-A	35.86	warning	-1.3	-8.27	6.6	40.71	OK	0.4	4.14	9.7	35.63			-8.87	
5th-A	84.29	Action	-6.5	-28.91	5.9	128.45	OK	0.9	8.34	8.5	103.46			-12.73	
6th-A	129.94	Action	-6.9	-31.82	6.2	209.96	warning	1.1	10.17	8.5	160.65			-15.70	
5th-B	87.90	Action	-5.3	-26.28	6.2	128.79	OK	0.8	8.01	8.8	102.78			-13.80	
4th-B	39.83	OK	-0.2	-1.82	7.3	41.17	OK	0.2	1.49	8.6	35.70			-12.00	
3rd-B	23.27	Action	2.0	14.48	6.1	20.25	OK	0.0	-0.41	9.5	19.61			-3.55	
2nd-B	14.38	Action	2.6	24.13	7.3	10.99	OK	-0.5	-5.08	10.0	11.89			2.63	
1st-B	5.31	Action	2.1	38.20	12.1	3.20	warning	-1.1	-16.61	16.9	3.80			-1.16	
		REE					LIKZ					AAA				
Toluene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %
1st-A	3.07	OK	-0.2	-6.12	10.0						3.61	OK	0.3	10.47	8.9
2nd-A	10.58	OK	-0.3	-3.18	10.1						11.39	OK	0.5	4.28	6.6
3rd-A	18.97	OK	-0.5	-2.79	9.0						20.32	OK	0.8	4.12	8.6
4th-A	38.84	OK	-0.3	-0.66	8.8						42.41	OK	3.3	8.49	7.8
5th-A	115.62	OK	-2.9	-2.48	8.8						116.63	OK	-1.9	-1.62	5.9
6th-A	184.80	OK	-5.8	-3.03	8.8						200.03	OK	9.5	4.96	5.9
5th-B	116.90	OK	-2.3	-1.96	8.7						113.84	OK	-5.4	-4.53	5.9
4th-B	40.50	OK	-0.1	-0.16	9.8						41.10	OK	0.5	1.32	5.9
3rd-B	20.51	OK	0.2	0.88	8.9						20.48	OK	0.1	0.72	6.2
2nd-B	11.55	OK	0.0	-0.29	9.5						12.21	OK	0.6	5.42	7.0
1st-B	3.79	OK	-0.1	-1.42	16.1						3.74	OK	-0.1	-2.80	9.7
		CHMI					LCSQA								
Toluene	Concentration, µg/m³	STATE	En	BIAS %	U %	Concentration, µg/m³	STATE	En	BIAS %	U %					
1st-A	2.85	OK	-0.4	-12.80	13.6	2.81	warning	-0.5	-13.94	8.5					
2nd-A	8.95	Action	-2.0	-18.07	9.3	10.35	OK	-0.6	-5.29	5.1					
3rd-A	16.05	Action	-3.5	-17.76	8.3	19.14	OK	-0.4	-1.96	4.6					
4th-A	32.55	Action	-6.5	-16.75	8.2	39.14	OK	0.1	0.13	4.5					
5th-A	103.24	Action	-15.3	-12.92	8.2	120.99	OK	2.4	2.05	4.6					
6th-A	163.13	Action	-27.4	-14.40	8.1										
5th-B	105.53	warning	-13.7	-11.49	8.8	121.68	OK	2.4	2.05	4.6					
4th-B	34.13	Action	-6.4	-15.88	11.1	39.90	OK	-0.7	-1.64	4.7					
3rd-B	16.66	Action	-3.7	-18.04	9.5	19.43	OK	-0.9	-4.45	4.6					
2nd-B	9.67	Action	-1.9	-16.52	9.4	10.72	warning	-0.9	-7.43	4.7					
1st-B	3.37	OK	-0.5	-12.36	18.3	3.02	Action	-0.8	-21.33	9.8					

U % values in red, correspond to reported data that did not pass the Repeatability score test

Table 12. E_n value, bias and reported expanded uncertainty of the participants: Ethyl-benzene

COMPOUND		HMS-1					HMS-2					ISCII				
Ethyl-benzene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.82	OK	-0.2	-6.3	18.9	0.69	OK	-0.9	-20.7	15.1					
2nd-A	2.01	OK	-0.9	-7.6	8.2	1.92	Action	-1.8	-11.9	6.2					
3rd-A	3.56	OK	-0.9	-6.1	5.3	3.48	warning	-1.0	-8.3	7.6					
4th-A	7.05	OK	-0.7	-3.4	3.9	7.72	warning	1.3	5.8	3.4					
5th-A	22.64	OK	1.0	3.8	3.2	22.57	OK	0.9	3.5	3.1					
6th-A	35.45	OK	0.1	0.5	3.2	36.28	OK	0.8	2.9	3.1					
5th-B	22.98	warning	1.1	4.1	3.2	22.62	OK	0.7	2.4	3.1					
4th-B	7.35	OK	-0.9	-4.7	4.4	7.81	OK	0.3	1.2	3.5					
3rd-B	3.74	OK	-0.8	-4.6	5.4	3.61	Action	-1.7	-8.0	4.3					
2nd-B	2.23	OK	-0.1	-2.3	17.0	1.98	Action	-2.1	-13.3	6.0					
1st-B	0.89	OK	-0.3	-5.6	17.6	0.73	warning	-1.4	-22.7	14.6					
COMPOUND		DLI					EKONERG					EEA				
Ethyl-benzene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.44	Action	-1.9	-49.4	31.8	0.51	Action	-1.9	-41.6	13.3					
2nd-A	1.36	Action	-4.7	-37.5	11.2	1.37	Action	-6.0	-37.1	7.7					
3rd-A	2.86	Action	-3.2	-24.5	8.2	3.05	Action	-3.3	-19.6	5.2					
4th-A	6.42	Action	-1.6	-12.1	8.2	6.13	Action	-3.5	-16.1	4.4					
5th-A	18.15	Action	-2.3	-16.8	8.3	18.66	Action	-3.6	-14.4	4.0					
6th-A	28.72	Action	-2.6	-18.5	8.3	30.64	Action	-3.4	-13.1	3.9					
5th-B	18.83	Action	-2.1	-14.7	8.2	19.08	Action	-3.6	-13.6	4.0					
4th-B	7.08	warning	-1.0	-8.2	8.2	6.39	Action	-3.1	-17.2	6.0					
3rd-B	3.29	Action	-2.1	-16.0	8.7	3.18	Action	-3.9	-18.8	5.2					
2nd-B	1.63	Action	-3.9	-28.5	8.9	1.70	warning	-1.5	-25.7	23.2					
1st-B	0.52	Action	-2.4	-45.4	28.3	0.58	Action	-2.7	-39.0	14.5					
COMPOUND		VMM-1					VMM-2					EPA				
Ethyl-benzene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.65	OK	-0.8	-25.93	34.9	0.44	Action	-2.4	-49.51	8.4	0.45			-48.67	
2nd-A	1.78	Action	-1.5	-18.31	13.8	1.29	Action	-6.0	-40.58	9.3	1.63			-25.04	
3rd-A	3.41	warning	-1.1	-10.06	9.5	2.35	Action	-5.2	-37.98	9.5	3.48			-8.31	
4th-A	7.57	OK	0.5	3.71	6.3	4.92	Action	-5.1	-32.54	8.5	7.59			3.91	
5th-A	22.21	OK	0.3	1.87	6.0	19.21	Action	-1.5	-11.89	8.4	21.53			-1.27	
6th-A	33.13	OK	-0.9	-6.02	6.7	31.30	warning	-1.4	-11.24	8.5	31.56			-10.48	
5th-B	23.27	OK	0.8	5.37	5.9	19.68	warning	-1.4	-10.88	8.6	21.66			-1.92	
4th-B	9.33	Action	1.9	21.02	9.1	5.23	Action	-4.9	-32.15	8.8	7.87			2.05	
3rd-B	4.50	OK	0.9	14.77	14.1	2.69	Action	-4.7	-31.37	9.1	3.68			-6.24	
2nd-B	2.37	OK	0.3	3.61	11.1	1.59	Action	-4.4	-30.48	8.4	1.96			-14.09	
1st-B	0.87	OK	-0.3	-8.52	26.2	0.63	Action	-2.5	-33.34	11.8	0.62			-34.12	
COMPOUND		REE					LIKZ					AAA				
Ethyl-benzene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.81	OK	-0.2	-7.65	47.8	0.50	Action	-1.6	-43.14	28.8					
2nd-A	2.08	OK	-0.3	-4.33	15.1	1.76	Action	-1.7	-19.16	13.4					
3rd-A	3.80	OK	0.0	0.17	15.7	3.54	OK	-0.6	-6.64	10.7					
4th-A	7.88	OK	0.4	7.90	16.2	6.94	OK	-0.5	-4.88	10.2					
5th-A	23.26	OK	0.6	6.69	10.9	20.61	OK	-0.6	-5.47	10.0					
6th-A	38.06	OK	0.7	7.93	11.0	34.13	OK	-0.3	-3.19	10.0					
5th-B	24.11	OK	0.7	9.16	11.5	20.55	OK	-0.7	-6.95	10.0					
4th-B	8.53	OK	0.7	10.56	13.7	6.99	OK	-1.0	-9.42	10.3					
3rd-B	4.19	OK	0.6	6.79	11.3	3.57	OK	-0.9	-9.00	10.7					
2nd-B	2.50	OK	0.5	9.23	16.9	1.84	Action	-1.8	-19.30	12.4					
1st-B	0.99	OK	0.2	4.80	16.8	0.55	Action	-2.1	-42.34	30.1					
COMPOUND		CHMI					LCSQA									
Ethyl-benzene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %					
1st-A	0.58	OK	-0.8	-33.48	55.8	0.63	warning	-1.3	-28.25	11.2					
2nd-A	1.67	warning	-1.3	-23.42	22.9	1.87	warning	-1.4	-14.11	10.8					
3rd-A	3.04	warning	-1.4	-19.77	16.5	3.58	OK	-0.8	-5.67	6.1					
4th-A	6.33	warning	-1.1	-13.27	13.8	7.38	OK	0.2	1.06	6.2					
5th-A	19.91	OK	-0.7	-8.69	13.6	22.82	OK	0.7	4.64	5.8					
6th-A	30.60	warning	-1.2	-13.20	12.8	37.23	OK	0.9	5.60	5.8					
5th-B	20.26	OK	-0.7	-8.27	13.6	23.12	OK	0.7	4.70	5.9					
4th-B	6.84	OK	-0.8	-11.28	15.9	7.58	OK	-0.2	-1.73	7.5					
3rd-B	3.43	OK	-0.9	-12.57	16.6	3.69	OK	-0.9	-5.77	6.1					
2nd-B	1.99	OK	-0.7	-12.79	20.7	2.04	warning	-1.0	-10.55	10.9					
1st-B	0.87	OK	-0.2	-8.77	40.1	0.67	Action	-2.2	-29.34	10.5					

U% values in red, correspond to reported data that did not pass the Repeatability score test

Table 13. E_n value, bias and reported expanded uncertainty of the participants: m,p-xylene

COMPOUND		HMS-1					HMS-2					ISCIII				
m,p-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.98	OK	-0.3	-9.2	21.8	0.75	warning	-1.1	-30.3	16.1					
2nd-A	2.12	OK	-0.9	-11.9	10.4	2.15	OK	-1.0	-10.6	6.4					
3rd-A	4.00	OK	-0.5	-4.0	5.9	3.66	Action	-2.0	-12.2	4.4					
4th-A	7.87	OK	-0.1	-0.5	4.1	8.31	warning	1.1	5.1	3.4					
5th-A	24.83	warning	1.1	4.7	3.4	25.61	Action	1.9	8.0	3.1					
6th-A	40.19	warning	1.1	4.7	3.3	41.10	Action	1.7	7.1	3.1					
5th-B	25.21	warning	1.0	4.3	3.2	25.64	warning	1.4	6.0	3.1					
4th-B	8.26	OK	-0.5	-2.7	4.5	8.41	OK	-0.2	-1.0	3.5					
3rd-B	4.21	OK	-0.5	-3.4	6.0	3.72	Action	-2.4	-14.6	4.4					
2nd-B	2.38	OK	-0.4	-8.7	24.3	2.23	Action	-1.6	-14.8	6.1					
1st-B	0.99	OK	-0.6	-16.3	21.2	0.76	Action	-1.6	-36.0	16.7					
COMPOUND		DLI					BKONERG					EEA				
m,p-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.43	Action	-2.0	-59.9	36.6	0.54	Action	-1.8	-50.3	19.8					
2nd-A	1.39	Action	-3.7	-42.3	12.0	1.38	Action	-4.2	-42.6	8.0					
3rd-A	3.10	Action	-3.1	-25.7	9.1	3.51	Action	-2.5	-15.9	5.0					
4th-A	7.21	warning	-1.0	-8.9	8.9	7.13	Action	-2.0	-9.9	4.5					
5th-A	20.16	Action	-1.9	-14.9	8.8	21.74	Action	-1.9	-8.3	4.0					
6th-A	29.68	Action	-3.2	-22.7	8.7	35.67	Action	-1.6	-7.0	3.9					
5th-B	20.95	Action	-1.7	-13.3	8.6	22.24	Action	-1.8	-8.0	4.0					
4th-B	8.29	OK	-0.3	-2.4	8.8	7.47	Action	-2.1	-12.1	5.6					
3rd-B	3.74	Action	-1.6	-14.3	9.1	3.70	Action	-2.4	-15.1	5.1					
2nd-B	1.80	Action	-3.2	-31.3	9.2	1.87	warning	-1.2	-28.6	32.0					
1st-B	0.55	Action	-2.2	-53.9	30.1	0.59	Action	-2.4	-50.6	16.1					
COMPOUND		VMM-1					VMM-2					EPA				
m,p-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	1.31	OK	0.4	21.13	44.3	0.54	Action	-1.8	-49.67	20.5	0.50			-53.74	
2nd-A	1.87	Action	-2.2	-22.43	6.5	1.53	Action	-3.2	-36.48	10.8	1.78			-26.09	
3rd-A	3.47	Action	-2.2	-16.76	7.0	2.75	Action	-4.6	-34.05	8.6	3.90			-6.35	
4th-A	7.57	OK	-0.6	-4.35	7.5	5.41	Action	-4.5	-31.65	9.4	8.74			10.42	
5th-A	23.78	OK	0.0	0.33	6.2	24.06	OK	0.2	1.51	8.5	24.34			2.69	
6th-A	37.35	OK	-0.4	-2.66	7.0	38.69	OK	0.1	0.83	8.5	34.53			-10.01	
5th-B	25.80	OK	1.0	6.70	6.1	24.56	OK	0.2	1.60	8.5	24.62			1.84	
4th-B	9.79	OK	1.0	15.26	13.5	5.75	Action	-4.3	-32.36	10.2	9.31			9.55	
3rd-B	4.81	warning	1.1	10.19	7.6	3.06	Action	-3.9	-29.91	8.6	4.20			-3.62	
2nd-B	2.82	OK	0.7	8.03	8.6	1.81	Action	-3.0	-30.79	9.7	2.21			-15.60	
1st-B	1.06	OK	-0.4	-10.67	22.9	0.71	Action	-1.7	-40.44	23.4	0.69			-41.65	
COMPOUND		REE					LIKZ					AAA				
m,p-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.99	OK	-0.1	-8.53	95.2	0.60	warning	-1.3	-44.60	38.4					
2nd-A	2.25	OK	-0.2	-6.60	42.8	2.11	OK	-0.8	-12.53	13.8					
3rd-A	4.06	OK	-0.2	-2.55	12.1	4.22	OK	0.1	1.34	7.9					
4th-A	8.34	OK	0.3	5.36	14.7	8.12	OK	0.3	2.53	6.6					
5th-A	23.51	OK	-0.1	-0.83	10.5	23.29	OK	-0.3	-1.75	6.0					
6th-A	37.60	OK	-0.2	-2.00	10.2	37.72	OK	-0.3	-1.71	5.9					
5th-B	24.49	OK	0.1	1.27	10.3	22.97	OK	-0.8	-4.98	6.0					
4th-B	9.27	OK	0.7	9.17	12.2	8.14	OK	-0.6	-4.19	7.1					
3rd-B	4.57	OK	0.4	4.79	10.9	4.16	OK	-0.5	-4.68	8.0					
2nd-B	2.69	OK	0.2	3.07	14.0	2.14	warning	-1.4	-18.15	12.4					
1st-B	1.08	OK	-0.1	-8.50	72.5	0.40	warning	-1.0	-65.96	182.1					
COMPOUND		CHMI					LCSQA								
m,p-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %					
1st-A	0.81	OK	-0.6	-25.16	40.1	0.72	warning	-1.2	-33.03	10.1					
2nd-A	1.84	warning	-1.3	-23.75	20.2	1.91	Action	-1.8	-20.77	8.7					
3rd-A	3.28	Action	-1.7	-21.24	15.2	3.78	OK	-0.9	-9.30	10.1					
4th-A	6.70	warning	-1.4	-15.41	12.3	8.34	OK	0.5	5.37	10.2					
5th-A	20.81	warning	-1.2	-12.22	11.4	27.57	Action	1.8	16.29	7.3					
6th-A	32.07	Action	-1.7	-16.43	11.3	46.16	Action	2.2	20.29	7.5					
5th-B	21.82	OK	-0.8	-9.76	12.6	28.23	Action	1.6	16.76	8.6					
4th-B	7.76	OK	-0.5	-8.67	17.9	8.65	OK	0.2	1.83	10.9					
3rd-B	3.93	OK	-0.7	-9.97	16.1	3.97	OK	-1.0	-9.07	8.9					
2nd-B	2.33	OK	-0.5	-10.91	21.1	2.11	Action	-1.6	-19.23	11.7					
1st-B	1.10	OK	-0.2	-7.40	34.0	0.69	Action	-1.8	-41.76	19.3					

U% values in red, correspond to reported data that did not pass the Repeatability score test

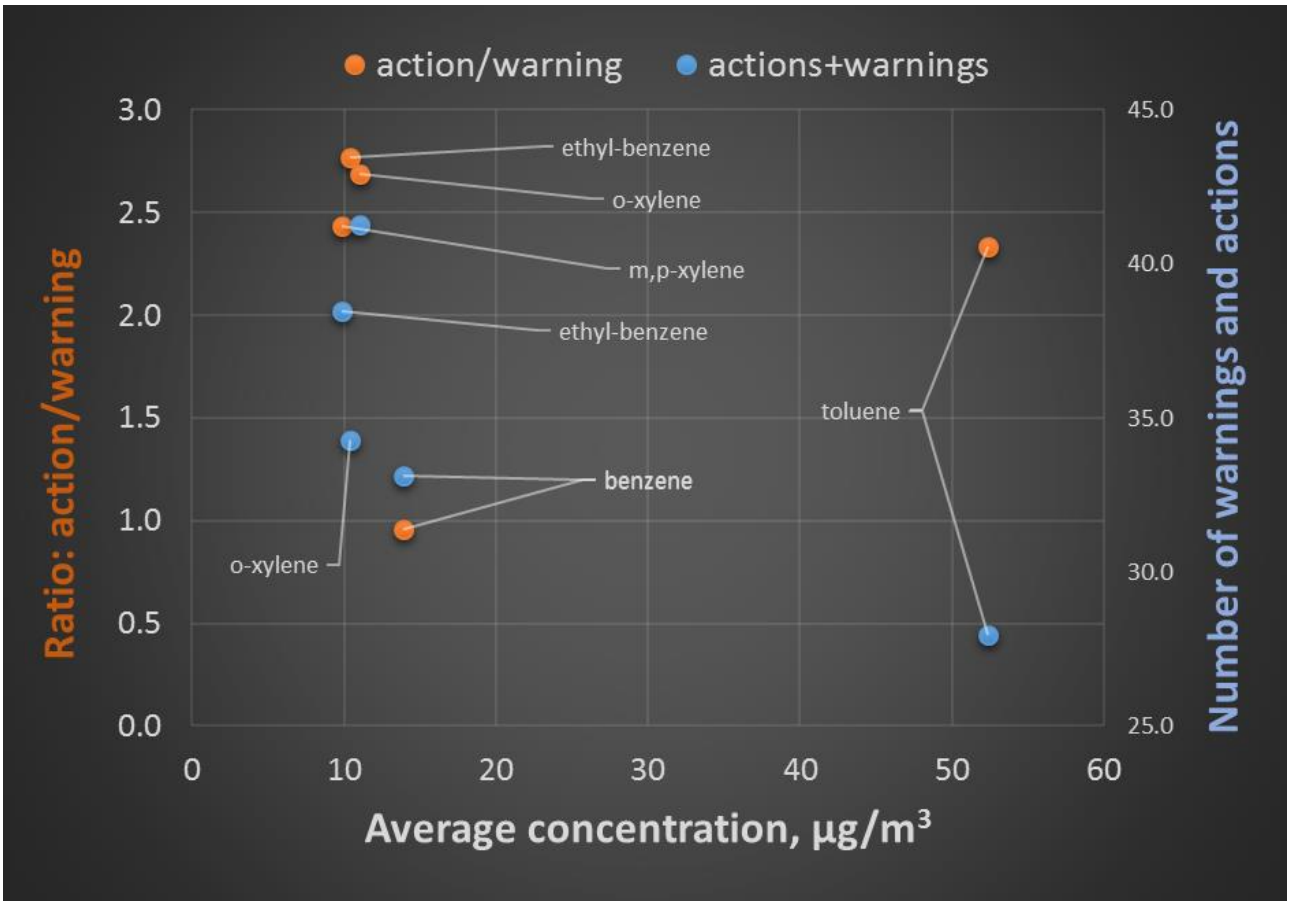
Table 14. E_n value, bias and reported expanded uncertainty of the participants: o-xylene

COMPOUND		HMS-1					HMS-2					ISCIII				
o-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %		Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.82	OK	-0.2	-7.4	16.9		0.68	OK	-0.8	-22.5	15.0					
2nd-A	2.09	warning	-1.1	-10.2	8.4		2.03	Action	-1.7	-12.8	5.9					
3rd-A	3.79	warning	-1.4	-8.0	4.7		3.80	warning	-1.4	-7.5	4.0					
4th-A	7.61	OK	-0.9	-4.6	4.4		8.18	OK	0.5	2.6	3.3					
5th-A	23.51	OK	-0.4	-1.4	3.4		24.51	OK	0.8	2.8	3.2					
6th-A	37.69	OK	-0.7	-2.8	3.3		39.11	OK	0.2	0.8	3.1					
5th-B	23.95	OK	-0.2	-0.7	3.2		24.90	OK	0.5	3.2	5.5					
4th-B	7.88	OK	-0.9	-6.6	7.4		8.29	OK	-0.4	-1.8	3.4					
3rd-B	4.08	OK	-0.9	-6.2	6.1		3.88	Action	-2.2	-10.7	4.1					
2nd-B	2.27	OK	-1.0	-10.1	9.8		2.14	Action	-2.1	-15.3	5.6					
1st-B	0.93	OK	-0.6	-11.0	15.2		0.73	Action	-2.0	-29.4	14.4					
COMPOUND		DLI					EKONERG					EEA				
o-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %		Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.64	OK	-0.8	-27.8	32.6		0.50	Action	-1.6	-42.9	13.7					
2nd-A	1.56	Action	-3.1	-33.0	13.3		1.61	Action	-2.6	-30.9	14.8					
3rd-A	3.21	Action	-2.0	-21.9	13.2		3.33	Action	-3.3	-19.0	5.2					
4th-A	7.47	OK	-0.5	-6.3	12.9		6.97	Action	-2.5	-12.6	4.5					
5th-A	19.39	Action	-1.7	-18.6	13.0		21.26	Action	-2.7	-10.8	4.1					
6th-A	32.43	warning	-1.5	-16.4	12.9		34.93	Action	-2.4	-9.9	4.0					
5th-B	20.37	warning	-1.4	-15.6	12.9		21.78	Action	-2.4	-9.7	4.0					
4th-B	8.38	OK	-0.1	-0.7	13.0		7.39	Action	-2.3	-12.4	5.4					
3rd-B	3.65	warning	-1.3	-16.0	13.6		3.54	Action	-3.2	-18.5	5.7					
2nd-B	1.80	Action	-2.4	-28.7	14.5		1.87	Action	-2.7	-26.0	10.5					
1st-B	0.60	Action	-1.9	-42.6	35.0		0.62	Action	-2.8	-40.9	15.9					
COMPOUND		VMM-1					VMM-2					EPA				
o-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %		Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.00						0.65	OK	-0.8	-26.60	29.7	0.64			-27.43	
2nd-A	1.73	warning	-1.0	-25.31	31.7		2.04	warning	-1.2	-12.00	8.8	2.50			7.60	
3rd-A	3.73	OK	-0.8	-9.25	11.2		3.93	OK	-0.5	-4.60	8.4	5.15			25.23	
4th-A	8.09	OK	0.2	1.35	8.0		7.91	OK	-0.1	-0.86	8.9	10.03			25.77	
5th-A	24.17	OK	0.2	1.39	6.1		24.73	OK	0.4	3.74	8.6	22.47			-5.73	
6th-A	36.19	warning	-1.0	-6.68	6.6		40.10	OK	0.4	3.40	8.6	35.29			-9.00	
5th-B	25.59	OK	0.9	6.09	6.2		25.03	OK	0.3	3.77	11.0	22.67			-6.01	
4th-B	10.20	Action	1.6	20.92	10.9		8.28	OK	-0.2	-1.90	9.4	10.30			22.05	
3rd-B	4.92	OK	0.6	13.26	19.9		4.13	OK	-0.6	-4.99	8.8	5.44			25.10	
2nd-B	2.51	OK	0.0	-0.39	11.0		2.25	OK	-0.8	-10.89	13.4	2.99			18.54	
1st-B	0.79	OK	-0.6	-23.71	51.3		0.82	Action	-1.5	-20.85	10.4	0.96			-8.17	
COMPOUND		REE					LIKZ					AAA				
o-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %		Concentration, µg/m3	STATE	En	BIAS %	U %	Concentration, µg/m3	STATE	En	BIAS %	U %
1st-A	0.84	OK	-0.1	-4.92	45.5		0.46	Action	-1.7	-48.36	16.2					
2nd-A	2.20	OK	-0.4	-5.22	12.7		1.76	Action	-2.4	-24.07	11.1					
3rd-A	4.10	OK	0.0	-0.42	8.9		3.74	OK	-1.0	-9.10	9.1					
4th-A	8.23	OK	0.3	3.22	8.4		7.80	OK	-0.2	-2.29	8.9					
5th-A	24.37	OK	0.2	2.24	9.7		23.74	OK	0.0	-0.41	8.9					
6th-A	39.39	OK	0.2	1.56	8.4		39.15	OK	0.1	0.95	8.8					
5th-B	25.62	OK	0.7	6.22	8.5		23.30	OK	-0.4	-3.42	8.8					
4th-B	9.34	OK	0.8	10.66	12.0		7.68	OK	-1.0	-8.93	9.4					
3rd-B	4.72	OK	0.8	8.57	9.2		3.62	Action	-2.0	-16.66	9.1					
2nd-B	2.65	OK	0.4	4.95	9.1		1.77	Action	-3.4	-30.07	9.7					
1st-B	1.06	OK	0.1	1.51	21.5		0.47	Action	-4.0	-64.66	18.1					
COMPOUND		CHMI					LCSQA									
o-Xylene	Concentration, µg/m3	STATE	En	BIAS %	U %		Concentration, µg/m3	STATE	En	BIAS %	U %					
1st-A	0.68	OK	-0.5	-23.01	50.3		0.56	warning	-1.3	-36.82	17.4					
2nd-A	1.75	warning	-1.4	-24.46	22.4		1.81	warning	-1.2	-22.07	21.8					
3rd-A	3.14	Action	-1.9	-23.66	15.6		3.24	Action	-2.3	-21.25	10.5					
4th-A	6.43	Action	-1.8	-19.42	12.6		6.78	Action	-1.7	-15.05	9.8					
5th-A	20.27	warning	-1.4	-14.98	12.8		21.83	OK	-0.9	-8.41	9.8					
6th-A	32.83	Action	-1.5	-15.35	11.5		37.34	OK	-0.4	-3.73	10.0					
5th-B	22.21	OK	-0.7	-7.93	12.6		22.29	OK	-0.8	-7.59	10.1					
4th-B	7.82	OK	-0.3	-7.31	22.7		7.10	Action	-1.6	-15.80	11.1					
3rd-B	3.90	OK	-0.6	-10.30	19.9		3.35	Action	-2.4	-23.02	11.6					
2nd-B	2.29	OK	-0.5	-9.09	21.2		1.90	Action	-1.5	-24.85	20.4					
1st-B	1.06	OK	0.1	2.18	39.6		0.62	Action	-2.4	-40.40	20.8					

U% values in red, correspond to reported data that did not pass the Repeatability score test

Figure 10 shows the variation of the average concentration with the total number of actions and warnings and their corresponding ratios for the exercise. It is clear that the number of total actions and warnings increased with the decrease of the analyte concentration. Such an effect was related to the difficulty of analysing these compounds at lower concentrations. A similar trend with respect to the concentration for the ratio action/warning was observed. Only toluene was outside this trend, showing a higher number of actions and ratios (action/warnings) than those expected from the level of the corresponding average concentration. This was because most of the actions and warnings appeared at the highest concentrations probably caused by the non-linear response of some of the detectors, reported measurements outside the calibration range or by cases of saturation of the trapping adsorbent.

Figure 10. Ratio and total number of actions and warnings for the inter-laboratory comparison exercise



4 Conclusions

The benzene reproducibility and repeatability standard deviation of the exercise at 5 µg/m^3 were circa 8 % and 3.8 %, respectively. These values were similar to the average reproducibility and repeatability standard deviation of the exercise, fulfilling the criteria for analytical robustness, $\gamma \leq 2$.

The reproducibility values were consistent with that expected from the standard deviation defined by N37 for proficiency assessment. Therefore, excluding outliers, the minimum standard deviation of the proficiency test was always lower than the standard deviation defined by the N37 for all the compounds and tested levels of concentration.

Most of the actions requested (E_n values >1.5) were documented for the C8 aromatic compounds at the lowest concentrations for which the uncertainties of the measurements became more pronounced. In the case of toluene, where higher concentrations were tested, actions were identified at the highest concentration levels due to possible non-linear detector response, calibrations out of measured range or saturation of the trapping adsorbent.

In comparison with the previous inter-laboratory comparison (EUR 27012 EN, 2014), a general improvement of the reproducibility, repeatability values and robustness, in particular the C8 aromatic compounds, was noted.

In view of future implementing actions (quality assurance for benzene and ozone precursor measurements) of the Directive 2008/50/EC, the analysis and reporting of C7 and C8 compounds during these inter-laboratory comparisons are highly recommended for participating laboratories.

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Annex:

Fourth EC-JRC aromatic compounds inter-laboratory comparison with automatic analysers

- Work schedule for the inter-laboratory comparison exercise
- Indicators of Mandel's statistic
- Robust Analysis: Estimation of robust values of the average and standard deviation of a number of inter-laboratory measurements
- Average repeatability, reproducibility and gamma values of 2nd and 3rd inter-laboratory exercise
- Conversion factors for data reporting
- Relative standard deviation, analytical uncertainty and uncertainty of the concentration level calculated for each laboratory
    - Benzene
    - Toluene
    - Ethyl-benzene
    - m,p-Xylene
    - o-Xylene
- Uncertainty of the reference value and overall inter-laboratory results
    - Benzene
    - Toluene
    - Ethyl-benzene
    - m,p-Xylene
    - o-Xylene
- Analysers and method description from participating laboratories

Work schedule for the inter-laboratory comparison exercise

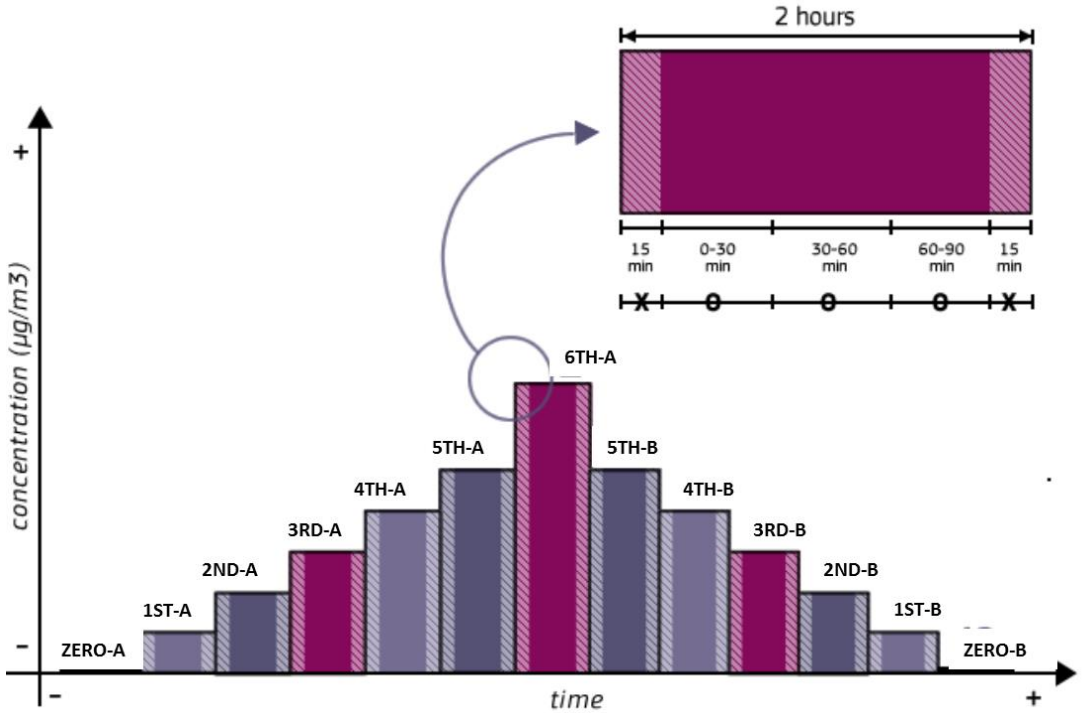
Sept. 19th: Arrival of participants and installation of equipment: 14:00 to 17:30

Sept. 20th: Calibration and Synchronization: : 9:00 – 13:30 / Measurements starting: 14:30

Sept. 21th: End of measurements: 15:30 / Calibration 15:30 – 17:30

Sept.22nd: Dismantling of equipment and departure of participants

Figure A-1. Time versus concentration steps along the exercise



Indicators of Mandel's statistic

Table A-1. k and h values

Number of Laboratories	k values at* of s.l.		h values at s.l.	
p	1 %	5 % **	1 %	5 % **
3	1.53	1.40	1.15	1.15
4	1.60	1.44	1.49	1.42
5	1.65	1.46	1.72	1.57
6	1.68	1.48	1.87	1.66
7	1.70	1.49	1.98	1.71
8	1.71	1.50	2.06	1.75
9	1.73	1.50	2.13	1.78
10	1.74	1.50	2.18	1.80
11	1.74	1.51	2.22	1.82
12	1.75	1.51	2.25	1.83
13	1.76	1.51	2.27	1.84
14	1.76	1.52	2.30	1.85
15	1.76	1.52	2.32	1.86
16	1.77	1.52	2.33	1.86
17	1.77	1.52	2.35	1.87
18	1.77	1.52	2.36	1.88
19	1.78	1.52	2.37	1.88
20	1.78	1.52	2.39	1.89
21	1.78	1.52	2.39	1.89
22	1.78	1.52	2.40	1.89
23	1.78	1.53	2.41	1.90
24	1.79	1.53	2.42	1.90
25	1.79	1.53	2.42	1.90
26	1.79	1.53	2.43	1.90
27	1.79	1.53	2.44	1.91

* for 5 replicated values. ** s.l. : significance level

Robust Analysis

Estimation of robust values of the average and standard deviation of a number of inter-laboratory measurements

The robust estimation of an average value, $\overline{C}_i^*$, and standard deviation, s*, of p inter-laboratory measurements is derived from a convergence process of the following equation:

$$\overline{C}_i^* = \frac{\sum C_i^*}{p}$$

Eq.A-1

$$s^* = 1.134 \cdot \sqrt{\frac{\sum (C_i - \overline{C}_i^*)^2}{(p-1)}}$$

Eq. A-2

Where recurrent values are calculated from these equations:

$$C_i^* = \begin{cases} \overline{C}_i^* - 1.5 \cdot s^* & \text{if} \quad C_i < \overline{C}_i^* - 1.5 \cdot s^* \\ \overline{C}_i^* + 1.5 \cdot s^* & \text{if} \quad C_i > \overline{C}_i^* + 1.5 \cdot s^* \\ C_i & \text{otherwise} \end{cases}$$

Eq. A-3

The initial values are calculated as:

$$\overline{C}_i^* = \text{median of } C_i \ (\text{i} = 1, 2, ...\text{p})$$
$$s^* = 1.483 \cdot \text{median of } \left| C_i - \overline{C}_i^* \right| (\text{i} = 1, 2, ...\text{p})$$

Eq. A-4

Overall results for the 2nd and 3rd inter-laboratory exercise

Average repeatability, reproducibility and gamma values

Table A-2. Average repeatability, reproducibility and gamma values for the 2nd inter-laboratory exercise

	Repeatability, %	**Reproducibility, %**	**Robustness (γ)**
Benzene	1.4	17.8	17.2
Toluene	1.8	10.0	7.1
Ethyl-benzene	2.2	9.7	6.1
m,p-Xylene	4.2	8.0	2.1
o-Xylene	3.1	16.5	6.7

(EUR 23792EN 2009)

Table A-3. Average repeatability, reproducibility and gamma values for the 3rd inter-laboratory exercise

	Repeatability, %	**Reproducibility, %**	**Robustness (γ)**
Benzene	4.7	7.9	1.7
Toluene	4.2	15.1	3.6
Ethyl-benzene	9.4	20.0	2.2
m,p-Xylene	9.3	26.6	2.8
o-Xylene	9.7	17.7	1.8

(EUR 27012EN 2014)

Conversion factors for data reporting

Table A-4. µg/m^3 to ppb (v/v) conversion factors

	Conversion factor µg/m^3 / ppb (v/v)
Benzene	3.25
Toluene	3.83
Ethyl-benzene	4.41
Xylenes	4.41

ppb(m/m) to ppb(v/v) factors were not taken into account.

Uncertainties and relative standard deviation (RSD) by laboratory

Figure A-2. Benzene: RSD, analytical uncertainty and U %

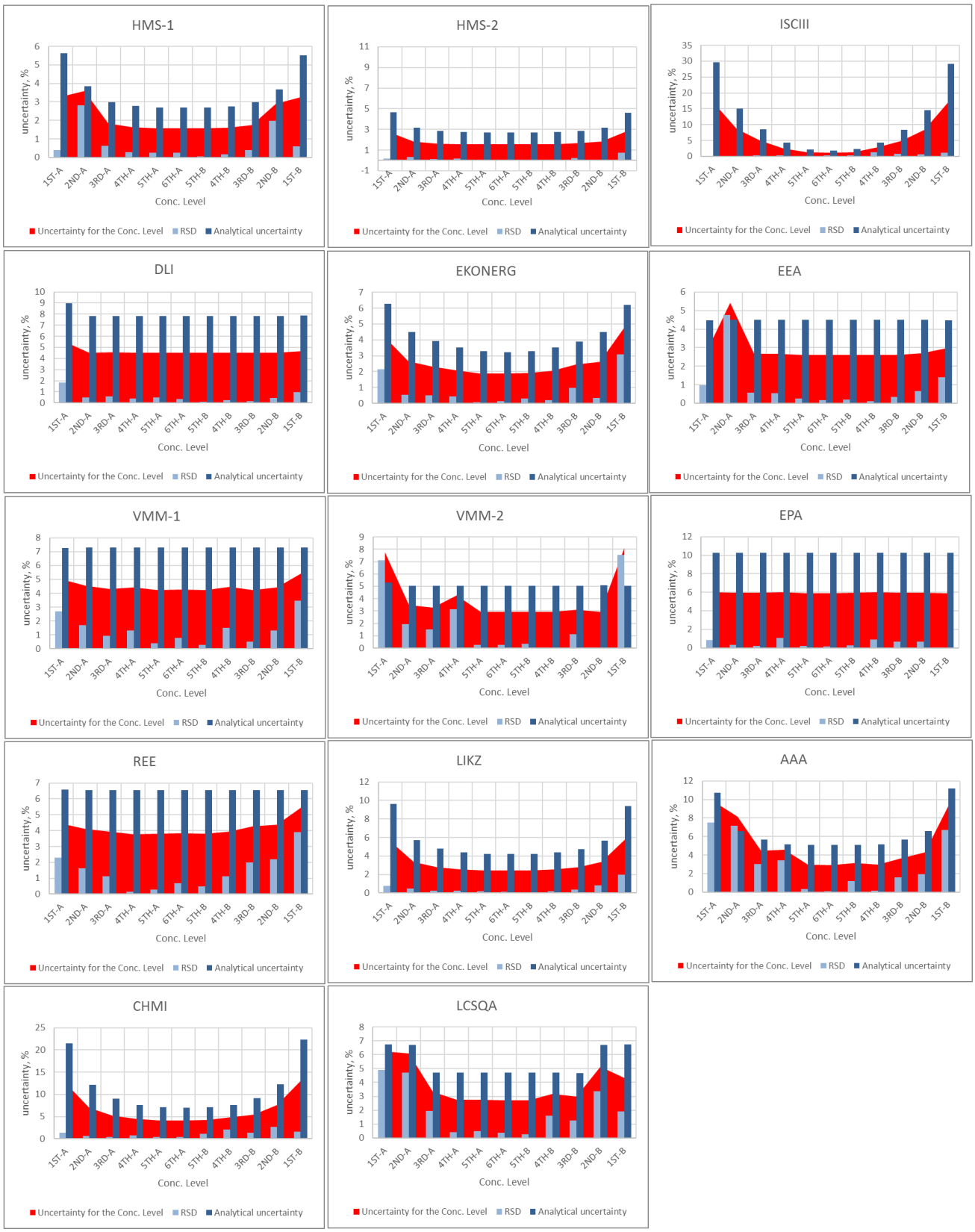


Figure A-3. Toluene: RSD, analytical uncertainty and U %

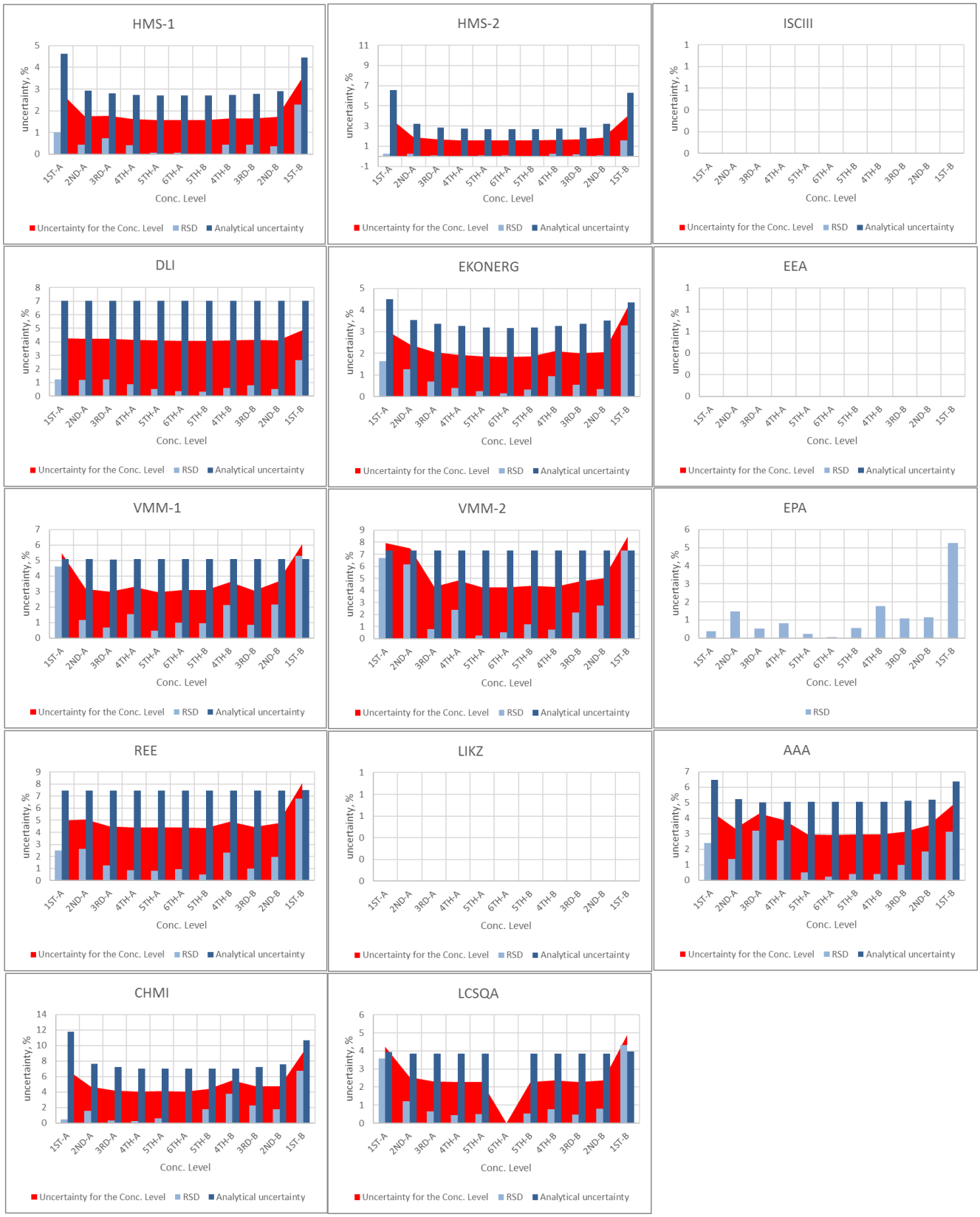


Figure A-4. Ethyl-benzene: RSD, analytical uncertainty and U %

Figure A-5. m,p-Xylene: RSD, analytical uncertainty and U %

Figure A-6. o-Xylene: RSD, analytical uncertainty and U %

Uncertainty of the reference value and overall inter-laboratory results

Figure A-7. Benzene: Repeatability reproducibility and reference value uncertainty

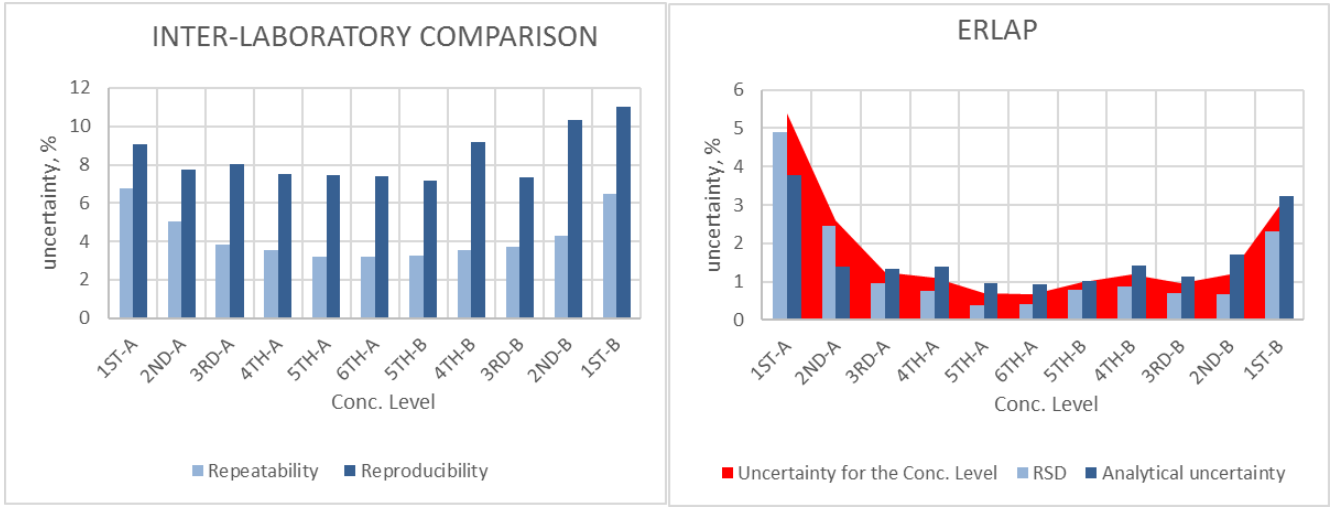


Figure A-8. Toluene: Repeatability reproducibility and reference value uncertainty

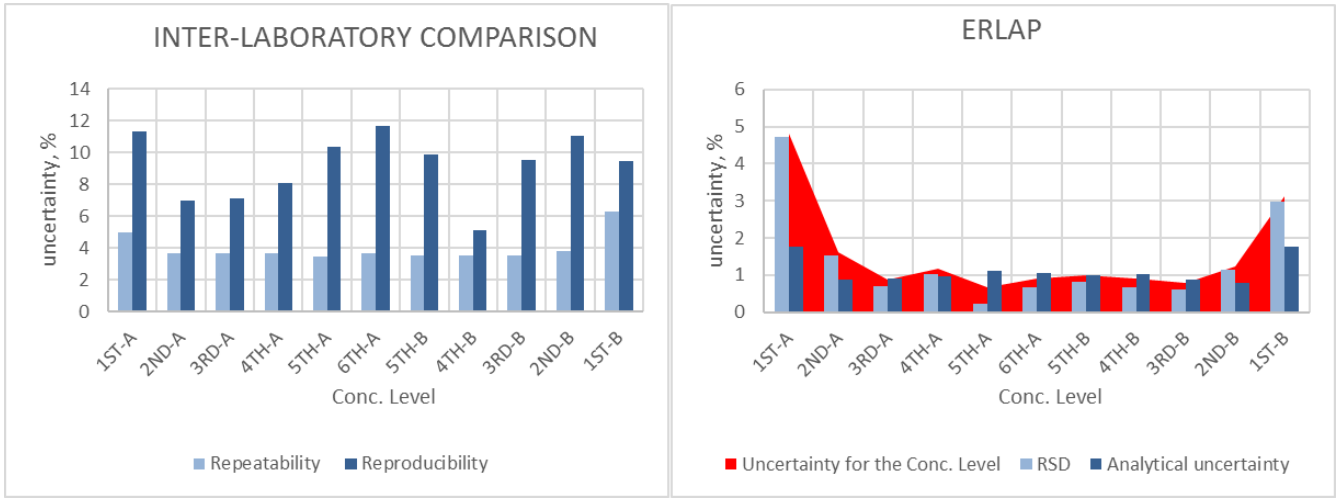


Figure A-9. Ethyl-benzene: Repeatability reproducibility and reference value uncertainty

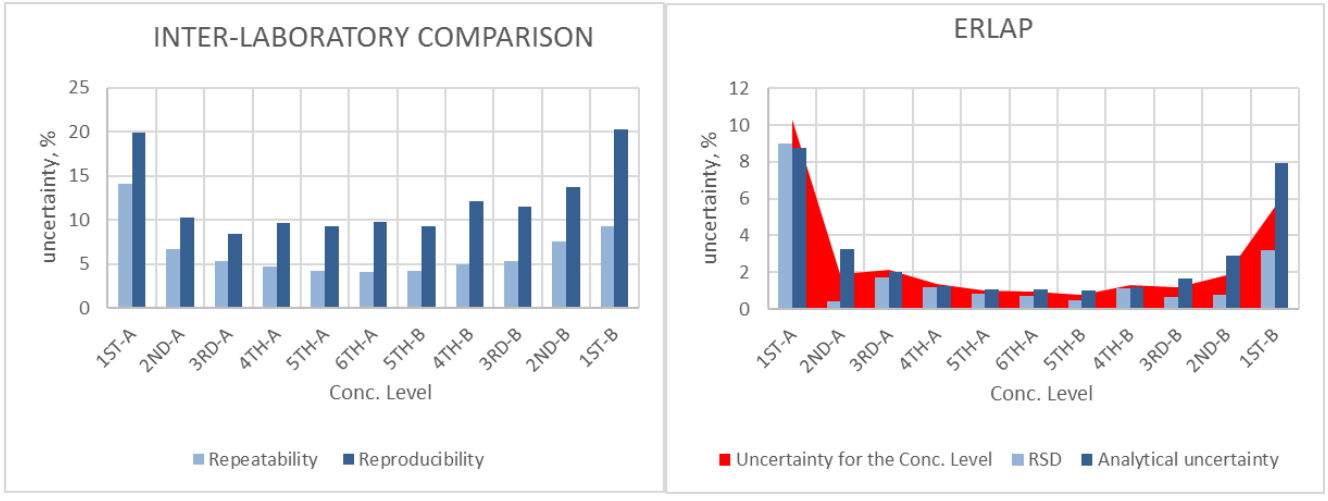


Figure A-10. m,p-Xylene: Repeatability reproducibility and reference value uncertainty

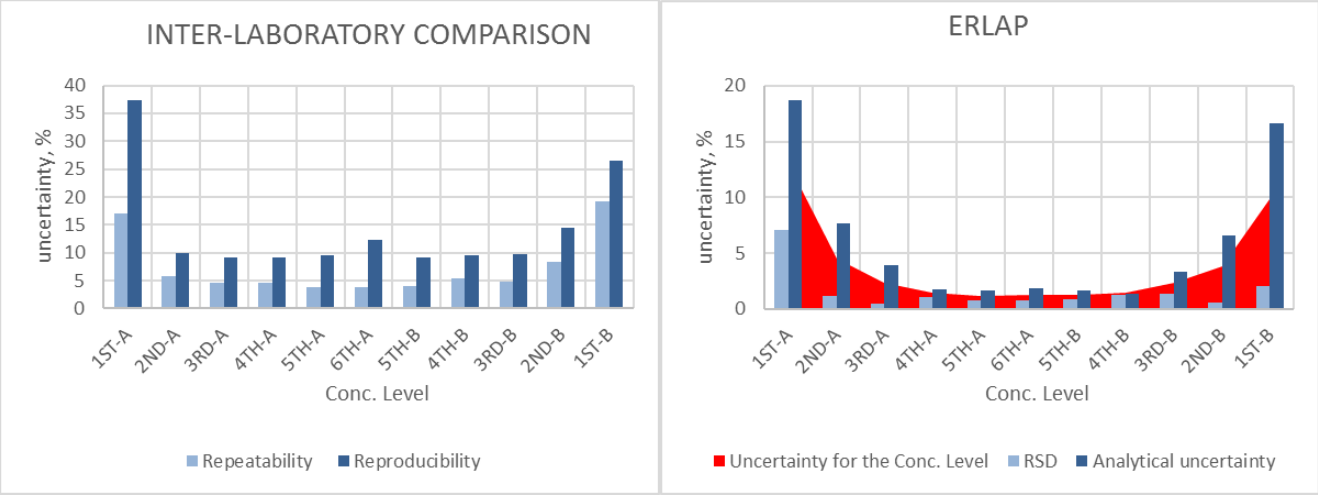
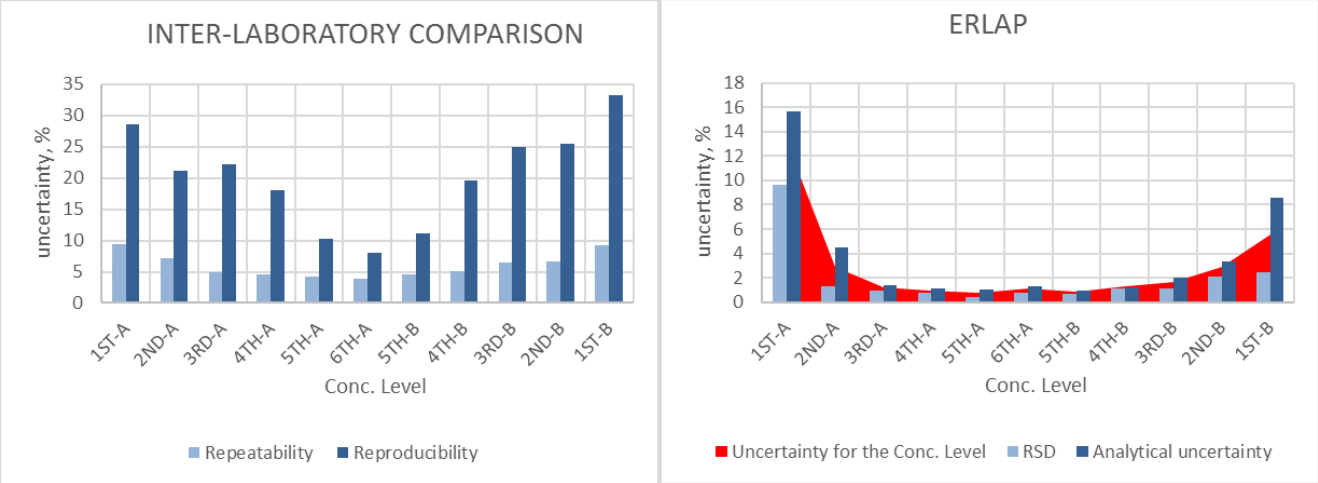


Figure A-11. o-Xylene: Repeatability reproducibility and reference value uncertainty



Analysers and method description from participating laboratories

HMS-1

HMS-2

ISCIII

DLI

EKONERG

EEA

VMM-1

VMM-2

EPA

REE

LIKZ

AAA

CHMI

LCSQA

ERLAP

HMS-1

Participating Laboratory	Air Quality Reference Centre, Hungarian Meteorological Service
Acronym	AQRC-HMS (LRK-OMSZ)
Person(s) responsible	Mr. Viktor DEZSI
Contact e-mails:	dezsi.v@met.hu
Telephone contact:	+36 20 3375762

Characteristic of your BTEX analyser

Trademark	Chromatotec/Airmotec
Model:	AirmoBTX
Version:	A31000
Year of manufacture:	2003

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:			YES		
Other gases used:					YES

Operating system:	Windows XP			
Cycle time, min:	30 min			
Adsorbent material:	MXT 30 CE			
Sampling control	pump			
Sampling temperature, °C	ambient			
Sample volume, ml	~415 ml			
Number of adsorbent tubes	3			
Desorption temperature, `	380			
Desorption time, sec	240			
Desorption flow, ml/min	3			
Cryo-trap detail				
Trapping temperature, °C	Ambient temperature			
Desorption temperature, °C	380	Desorption time, sec		
Desorption flow, ml/min		split flow, ml/min		
Stripper column				
Analytical column	MXT 30 CE			
phase:				
length, m:	30			
diameter (ID) mm:	0.28			
thickness (µm):	1			
analytical conditions:	start 36°C, gradiant 2°C/min to 38°C (duration 60 s), gradiant 2°C/min to 50°C (duration 360 s), gradiant 10°C/min to 80°C (duration 180 s), gradiant 15°C/min to 200°C (duration 480 s), Isotherm 200°C up to 300 s, decrease to 36°C,			

Traceability of your calibration Standard

Certified reference material (CRM):	VSL Dutch Metrology Institute	
Certified by	VSL Dutch Metrology Institute	
Certified number:	3222603	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	965	29
Toluene	990	30
Ethyl-benzene	969	29
m-Xylene	979	29
p-Xylene	983	29
o-Xylene	996	30

Other methods	
Dilution of CRM	
Static Injection	
Permeation	
Additional comments	

HMS-2

Participating Laboratory	Air Quality Reference Centre, Hungarian Meteorological Service
Acronym	AQRC-HMS (LRK-OMSZ)
Person(s) responsible	Mr. Viktor DEZSI
Contact e-mails:	dezsi.v@met.hu
Telephone contact:	+36 20 3375762

Characteristic of your BTEX analyser

Trademark	Environnement sa
Model:	VOC 72M
Version:	
Year of manufacture:	2014

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		YES			
Other gases used:					

Operating system:	DNP-ARM7 version 3.3.8
Cycle time, min:	15 min
Adsorbent material:	
Sampling control	
Sampling temperature, °C	ambient
Sample volume, ml	165
Number of adsorbent tubes	1
Desorption temperature, `	380
Desorption time, sec	2
Desorption flow, ml/min	12
Cryo-trap detail	
Trapping temperature, °C	380
Desorption temperature, °C	Desorption time, sec
Desorption flow, ml/min	split flow, ml/min
Stripper column	
Analytical column	Stainless steel
phase:	a-polar
length, m:	15
diameter (ID) mm:	0.25
thickness (µm):	1
analytical conditions:	ht 15°C/min to 115°C (duration 420 s), gradiant 30°C/min to 160°C (duration 120

Traceability of your calibration Standard

Certified reference material (CRM):	VSL Dutch Metrology Institute
Certified by	VSL Dutch Metrology Institute
Certified number:	3222603

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	965	29
Toluene	990	30
Ethyl-benzene	969	29
m-Xylene	979	29
p-Xylene	983	29
o-Xylene	996	30

Other methods	
Dilution of CRM	
Static Injection	
Permeation	
Additional comments	

száma: s50.1/2016

Országos Meteorológiai Szolgálat
Éghajlati és Levegőkörnyezeti Főosztály
Levegőtisztaság-védelmi Referencia Központ
Kalibráló Laboratórium
Központ: 1024 Budapest, Kitaibel Pál u. 1.
Telephely: 1181. Budapest, Gilice tér 39.
Telefon: 346-4800
Telefax: 346-4647

A NAT által NAT-2-0285/2014 számon akkreditált kalibrálólaboratórium

KALIBRÁLÁSI BIZONYÍTVÁNY

száma: s50.1/2016

Mérőeszköz megnevezése:	BTEX (C6-C12) gázelemző
Típusa:	A31000
Gyártó:	Airmotec
Gyári száma:	2020100
A megrendelő neve:	OMSZ ÉLFO LRK Kalibráló Laboratórium
Kalibrálás helye:	OMSZ ÉLFO LRK Kalibráló Laboratórium
Kalibrálás ideje:	2016.08.29-08.31.
Kalibrálás módszere:	Minőségirányítási Kézikönyvben rögzített "B1" módszer - (gázkeverő berendezés alkalmazásával, tanúsított anyagminta felhasználásával) azonosító: K.E-5.4-B1-2014-V.4
Kalibrálás körülményei:	környezeti hőmérséklet: 21,5 °C légköri nyomás: 1001 hPa

Kalibrálást végezte: dr. Machon Attila

száma: s50.1/2016

Országos Meteorológiai Szolgálat
Éghajlati és Levegőkörnyezeti Főosztály
Levegőtisztaság-védelmi Referencia Központ
Kalibráló Laboratórium

A NAT által NAT-2-0285/2014 számon akkreditált kalibrálólaboratórium

A kalibrálásnál alkalmazott tanúsított anyagminták és kalibráló berendezések visszavezetettsége hitelesítéssel, illetve kalibrálással biztosított:

Gázkeverő készülék: típ.: MCZ RLAB, azonosító sz.: 0211-0212, Mjk. sz.: s02/2016;
VOC/N_2 1 ppm ± 0,05 ppm (n/n), palackszám: MS7313, Kal. biz. sz.: VSL 3222603 [PRM];
Univerzális hőmérséklet- és nyomásmérő: típ.: Almemo 2290-3, gy.sz.: 942911;
Digitális hőmérő: típ.: Almemo ZA 9030-FS1, Kal. jk. sz.: KM/2015/0827-02;
Légnyomásmérő: típ. : Druck FD A612-MA, gy. sz.: 00110403, Kal. jk. sz.: KM/2015/0827-01;
Segédanyag: '0'-levegő, nullgáz generátorral előállítva.

Mérési eredmények:

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*	
		'0'-levegő	0,04	ppb	-	
2,911	ppb	**benzol**/N_2:lev.	2,89	ppb	0,10	ppb
5,826	ppb	"	5,81	ppb	0,20	ppb
8,708	ppb	"	8,67	ppb	0,31	ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*	
		'0'-levegő	0,1	ppb	-	
2,986	ppb	**toluol**/N_2:lev.	2,92	ppb	0,11	ppb
5,976	ppb	"	5,99	ppb	0,21	ppb
8,933	ppb	"	8,95	ppb	0,32	ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*	
		'0'-levegő	0,19	ppb	-	
2,923	ppb	**etil-benzol**/N_2:lev	2,85	ppb	0,10	ppb
5,850	ppb	"	5,87	ppb	0,20	ppb
8,744	ppb	"	8,70	ppb	0,31	ppb

Kalibrálást végezte: dr. Machon Attila

száma: s50.1/2016

Országos Meteorológiai Szolgálat
Éghajlati és Levegőkörnyezeti Főosztály
Levegőtisztaság-védelmi Referencia Központ
Kalibráló Laboratórium

A NAT által NAT-2-0285/2014 számon akkreditált kalibrálólaboratórium

Mérési eredmények (folytatás):

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*	
		'0'-levegő	0,51	ppb	-	
5,918	ppb	**m-p-xilol**/N_2:lev	5,55	ppb	0,21	ppb
11,844	ppb	"	11,66	ppb	0,41	ppb
17,704	ppb	"	17,57	ppb	0,61	ppb

Kalibráló gáz (n/n)			Mért értékek átlaga (n/n)		Mérési bizonytalanság (U)*	
		'0'-levegő	0,23	ppb	-	
3,004	ppb	**o-xilol**/N_2:lev.	2,68	ppb	0,11	ppb
5,976	ppb	"	5,74	ppb	0,21	ppb
8,987	ppb	"	8,92	ppb	0,32	ppb

* A kalibrálás U kiterjesztett bizonytalansága az EA-4/02 dokumentumnak megfelelően az u(y) eredő standard bizonytalanságnak a k = 2 kiterjesztési tényezővel szorzott értéke, ami normális eloszlás esetén közelítőleg 95% fedési valószínűségnek felel meg.

Megjegyzés:

- A kalibrálás eredménye a talált metrológiai jellemzőket rögzíti.
- Kalibrálás alatt a készülék az alábbi beállításokkal rendelkezett:

Mérési program:	AMB-15MN	
Retenciós tábla:	BTEX15F3	
Minta térfogata (Sample volume):	~420	ml
FID hőm.:	170,0	°C
Érzékenység (Base sensitivity):	5560,0	
Detektor jel erősítés (Amplification level):	3-High	

Kiállítás kelte: Budapest, 2016.09.05.

Kiadható:

Kalibrálást végezte: dr. Machon Attila

Dézsi Viktor
osztályvezető

Készült 1 példányban. A jelen bizonyítvány csak teljes formájában és terjedelmében érvényes és másolható.

3/3 oldal

Participating Laboratory	INSTITUTO DE SALUD CARLOS III
Acronym	ISCIII
Person(s) responsible	Rosalia+ Fernandez Patier
Contact e-mails:	pmorillo@isciii.es; rosalia.fernandez@isciii.es
Telephone contact:	

ISCIII

Characteristic of your BTEX analyser

Trademark	SYNTECH SPECTRAS				
Model:	GC955				
Version:					
Year of manufacture:	2004				
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		X			
Other gases used:					
Operating system:	WINDOWS				
Cycle time, min:	15 min				
Adsorbent material:	Tenax GR 60-80				
Sampling control	pump/MFC/piston				
Sampling temperature, °C	≈ 25 °C				
Sample volume, ml	50 ml				
Number of adsorbent tubes	--				
Desorption temperature, `	5 °C - 35 °C				
Desorption time, sec					
Desorption flow, ml/min					
Cryo-trap detail	--				
Trapping temperature, °C					
Desorption temperature, °C	180 °C	Desorption time, sec	40 s		
Desorption flow, ml/min	1,5 ml/min	split flow, ml/min			
Stripper column	dimetil-polixiloxano (94 %) and ciano-propil-fenilo (6 %); 2 m				
Analytical column	AT-624				
phase:	dimetil-polixiloxano (94 %) and ciano-propil-fenilo (6 %)				
length, m:	13 m				
diameter (ID) mm:	0,32 mm				
thickness (µm):	1,8 µm				
analytical conditions:	50°C (3'),10°C/min,70°C (6'), 10°C/min 50°C				

Traceability of your calibration Standard

Certified reference material (CRM):	VSL	
Certified by	VSL	
Certified number:		
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	503	15
Toluene	501	15
Ethyl-benzene	505	15
m-Xylene	491	15
p-Xylene	498	15
o-Xylene	504	15
Other methods		
Dilution of CRM	API 700	
Static Injection		
Permeation		
Additional comments		

VSL
Dutch
Metrology
Institute

ZA-00-22

ISCIII

CERTIFICATE

Number 3222892

Reference material of BTEX

Description: Primary reference gas mixture (PRM), cylinder number APEX1161130.
The cylinder contains a mixture of BTEX in nitrogen.
The PRM is contained in a passivated aluminium cylinder. The cylinder has a water volume of 5 L and is pressurized to 11.9 MPa.
Cylinder outlet conforms to DIN 1 specifications.

Method of preparation: Gravimetric preparation in accordance with ISO 6142:2001 (*Gas analysis - Preparation of calibration gas mixtures - Gravimetric method*).

Result

Component	Amount fraction [mol/mol]	Uncertainty [mol/mol]
benzene	503×10^{-9}	15×10^{-9}
toluene	501×10^{-9}	15×10^{-9}
ethylbenzene	505×10^{-9}	15×10^{-9}
o-xylene	491×10^{-9}	15×10^{-9}
m-xylene	498×10^{-9}	15×10^{-9}
p-xylene	504×10^{-9}	15×10^{-9}

The reported uncertainty of measurement is based on the standard uncertainty multiplied by a coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard uncertainty has been determined in accordance with the GUM '*Evaluation of measurement data - Guide to the Expression of Uncertainty in Measurement*'.

Traceability: The values on this certificate are traceable to VSL Primary Standards.

Safety information: The cylinder should be handled with care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of gaseous materials.

Instructions for use: The material can be used to validate and/or calibrate analytical methods applied.

Do not use the cylinder in case the cylinder pressure is below 1 MPa.
More instructions can be found in ISO 16664:2004 (*Gas analysis – Handling of calibration gases and gas mixtures – Guidelines*).

Expiry date: The certificate is valid until 14 October 2018.

Delft, 4 November 2015
VSL B.V.

J.I.T. van Wijk
Senior Metrologist

VSL
Dutch
Metrology
Institute

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I www.vsl.nl

BTEX analysers Inter-laboratory comparison
19- 22 September 2016
JRC Ispra (ERLAP)

DLI

Participating Laboratory	Air Quality Section, Department of Labour Inspection
Acronym	AQS DLI
Person(s) responsible	Christos Kizas & Christos Papadopoulos
Contact e-mails:	ckizas@dli.mlsi.gov.cy, cpapadopoulos@dli.mlsi.gov.cy
Telephone contact:	00357-22-405674, 00357-22-405683

Characteristic of your BTEX analyser

Trademark	Synspec
Model:	GC955
Version:	600
Year of manufacture:	2008

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		X			
Other gases used:					

Operating system:	Windows Xpe
Cycle time, min:	15 min
Adsorbent material:	TENAX GR 60/80 mesh, 8 cm
Sampling control	Sampling Cylinder
Sampling temperature, °C	Ambient
Sample volume, ml	93
Number of adsorbent tubes	1
Desorption temperature, `	180
Desorption time, sec	15 - 60
Desorption flow, ml/min	1.4
Cryo-trap detail	
Trapping temperature, °C	
Desorption temperature, °C	Desorption time, sec
Desorption flow, ml/min	split flow, ml/min
Stripper column	e: 95% dimethylpolysiloxane, 5% diphenylpolysiloxane, Length: 2m, Diameter
Analytical column	AT-5
phase:	95% dimethylpolysiloxane, 5% diphenylpolysiloxane
length, m:	13
diameter (ID) mm:	0.32
thickness (µm):	1
analytical conditions:	Initial 50°C, 3'-4' ramp from 50°C to 80°C, 4'-12' constant at 80°C, 12'-14' ramp from 80°C to 50°C

Traceability of your calibration Standard

Certified reference material (CRM):	VSL Primary Reference Gas Mixture (BTEX in nitrogen)
Certified by	VSL, Dutch Metrology Institute
Certified number:	3222779.04

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	677 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
Toluene	675 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
Ethyl-benzene	680 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
m-Xylene	670 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
p-Xylene	679 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
o-Xylene	661 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol

Other methods	
Dilution of CRM	Sabio 4010, Range: ~ 1 - 20 ppb
Static Injection	
Permeation	
Additional comments	

VSL
Dutch Metrology Institute

DLI

CERTIFICATE

Number 3222779.04
Page 1 of 1

Reference material of BTEX in nitrogen

Description: Primary reference gas mixture (PRM), cylinder number APEX1099178.
The cylinder contains a mixture of BTEX in nitrogen.
The PRM is contained in a passivated aluminium cylinder. The cylinder has a water volume of 5 L and is pressurized to 12.4 MPa.
Cylinder outlet conforms to DIN 1 specifications.

Method of preparation: Gravimetric preparation in accordance with ISO 6142:2001 (*Gas analysis - Preparation of calibration gas mixtures - Gravimetric method*).

Result

Component	Amount fraction [mol/mol]	Uncertainty [mol/mol]
benzene	677×10^{-9}	20×10^{-9}
toluene	675×10^{-9}	20×10^{-9}
ethylbenzene	680×10^{-9}	20×10^{-9}
o-xylene	661×10^{-9}	20×10^{-9}
m-xylene	670×10^{-9}	20×10^{-9}
p-xylene	679×10^{-9}	20×10^{-9}

The reported uncertainty of measurement is based on the standard uncertainty multiplied by a coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard uncertainty has been determined in accordance with the GUM '*Evaluation of measurement data - Guide to the Expression of Uncertainty in Measurement*'.

Traceability: The values on this certificate are traceable to VSL Primary Standards.

Safety information: The cylinder should be handled with care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of gaseous materials.

Instructions for use: The material can be used to validate and/or calibrate analytical methods applied.

Do not use the cylinder in case the cylinder pressure is below 1 MPa.
More instructions can be found in ISO 16664:2004 (*Gas analysis – Handling of calibration gases and gas mixtures – Guidelines*).

Expiry date: The certificate is valid until 8 April 2018.

Delft, 4 June 2015
VSL B.V.

J.I.T. van Wijk
Senior Metrologist

VSL Dutch Metrology Institute

This certificate is consistent with Calibration and Measurement Capabilities (CMCs) that are included in Appendix C of the Mutual Recognition Arrangement (MRA) drawn up by the International Committee for Weights and Measures (CIPM). Under the MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://kcdb.bipm.fr).

CIPM MRA

VSL B.V.
Thijsseweg 11, 2629 JA Delft (NL)
P.O. Box 654, 2600 AR Delft (NL)
T +31 15 269 15 00
F +31 15 261 29 71
I www.vsl.nl

EKONERG

Participating Laboratory	EKONERG				
Acronym					
Person(s) responsible	Predrag Hercog				
Contact e-mails:	predrag.hercog@ekonerg.hr				
Telephone contact:					
Characteristic of your BTEX analyser					
Trademark					
Model:	**Chromatotec airmoVOC**				
Version:	**GC 866**				
Year of manufacture:	2014				
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:			Yes		
Other gases used:					Yes
Operating system:	Windows XP / Vistachrom 1.49				
Cycle time, min:	15				
Adsorbent material:	CarboTRAP				
Sampling control	pump/critical orifice				
Sampling temperature, °CSampli	Ambient temperature				
Sample volume, ml	470				
Number of adsorbent tubes	1				
Desorption temperature, `	380 C				
Desorption time, sec	120				
Desorption flow, ml/min					
Cryo-trap detail					
Trapping temperature, °C	Ambient temperature				
Desorption temperature, °C	380 C	Desorption time, sec			
Desorption flow, ml/min		split flow, ml/min			
Stripper column					
Analytical column	MXT 30 CE				
phase:	metallic film				
length, m:	30				
diameter (ID) mm:	0.28				
thickness (µm):	1				
analytical conditions:	0-60sec ramp 2 C/min starting from 44 up to 45C, 60-540sec ramp 15 C/min up to 165C, 540-660sec keep 165C constant, 660sec-900sec cooling				
Traceability of your calibration Standard					
Certified reference material (CRM):	NPL (PRM)				
Certified by	NPL				
Certified number:	D09 0592				
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)			
Benzene	12.14	0.24			
Toluene	12.3	0.31			
Ethyl-benzene	11.61	0.29			
m-Xylene	12.21	0.31			
p-Xylene	11.75	0.30			
o-Xylene	12.28	0.31			
Other methods					
Dilution of CRM					
Static Injection					
Permeation					
Additional comments					

EKONERG d.o.o.✦Odjel za mjerenja i analitiku
Umjerni laboratorij, Koranska 5, HR-10000 Zagreb
Tel: +385 (0)1 6000-111; **Faks**: +385 (0)1 6171-560

17025 HAA
2471

POTVRDA O UMJERAVANJU
CALIBRATION CERTIFICATE

Br./No. 97/2016

Radni nalog Work order	**I-02-3024/16**
Kupac Customer	**Ekonerg d.o.o., Umjerni laboratorij**
Adresa kupca Customer address	Koranska 5, HR-10000 Zagreb
Naziv analizatora Calibrated analyzer	Analizator benzena
Proizvođač Manufacturer	CHROMATOTEC
Tip Type	airTOXIC GC 866 (UM-REF-06)
Serijski broj Serial number	23140414
Veličina Quantity	Koncentracija C_6H_6 / µg/m^3
Mjerno područje Measurement range	0 – 50 µg/m^3 (0 – 15 nmol/mol)
Stanje analizatora Description of analyzer	Ispravan
Datum umjeravanja Date of calibration	2016-06-24
Umjeravanje proveo Calibration provided by	Predrag Hercog

Broj stranica Number of pages	**5**	**Datum izdanja** Date of issue	**2016-07-06**

Voditelj Umjernog laboratorija *Head of Calibration Laboratory*	Direktor Odjela za mjerenja i analitiku *Director of MA Department*
Zlatko Grgić, dipl. ing.univ.spec.	Bojan Abramović, dipl. ing.

1. POSTUPAK UMJERAVANJA
CALIBRATION PROCEDURE

Umjeravanje je provedeno izravnim postupkom umjeravanja u nekoliko točaka opisanim u protokolu eLAB-PU-101, *Umjeravanje imisijskih analizatora*, izdanje 5, 2016-02-11, točka 3.5.5. Provjera funkcionalnosti provedena je sukladno istom protokolu, točka 3.4. Referentna koncentracija C_6H_6 u nmol/mol dobiva se dinamičkim razrjeđivanjem certificiranog referentnog plina na željenu vrijednost pomoću umjerenog kalibratora.

Calibration was performed by direct calibration procedure at several points as described in the protocol eLAB-PU-101, Calibration of imission analyzer, issue 5, 2016-02-11, clause 3.5.5. Functional tests are provided according to the same protocol, clause 3.4. Reference C_6H_6 concentration in nmol/mol is obtained by dynamic dilution of certified reference gas to the desired value using calibrated dilution unit.

2. OPREMA ZA UMJERAVANJE I MJERNA SLJEDIVOST
CALIBRATION EQUIPMENT AND MEASUREMENT TRACEABILITY

2.1 **OPREMA** / *EQUIPMENT*

Oprema ili materijal *Equipment or material*	Namjena *Purpose*	Proizvođač *Manufacturer*
Certificirani referentni plin *Certified reference gas* [RPI-C6H6/9.15]	Izvor točne koncentracije referentnog plina. *Source of accurate concentration of the reference gas.*	BOC (Linde Group)
Sustav za dobivanje nultog zraka *Zero gas generator* [UM-GNZ1]	Izvor nultog plina. *Source of the zero gas.*	Horiba
Referentni kalibrator *Reference dilution unit* [UM-KAL1]	Miješanje certificiranog referentnog plina i nultog plina u točno određenim odnosima radi dobivanja točne koncentracije referentnog plina. *Blending certified reference gas and zero gas to obtain accurate concentration of the reference gas.*	Horiba
Termohigrometar *Thermo-hygrometer* [UM-THM2]	Praćenje temperature i vlažnosti u laboratoriju. *Monitoring of temperature and humidity in the laboratory.*	Rense
Tlakomjer *Pressure gauge* [UM-TLK]	Praćenje tlaka u laboratoriju. *Monitoring of pressure in the laboratory.*	Wika

2.2 **MJERNA SLJEDIVOST OPREME** / *MEASUREMENT TRACEABILITY OF THE EQUIPMENT*

Oprema ili materijal *Equipment or material*	Sljedivost *Traceability*
Certificirani referentni plin *Certified reference gas*	Hungarian Meteorological Service, Calibration Certificate No.188/15, 2015-11-11
Referentni kalibrator *Reference dilutor unit*	ČMI, Certificate of Calibration 6013-KL-M0223-16, 2016-05-12 ČMI, Certificate of Calibration 6013-KL-M0224-16, 2016-05-12

3. REZULTATI
RESULTS

3.1 UVJETI OKOLIŠA / *AMBIENT CONDITIONS*

Temperatura zraka / *Air Temperature*:	24°C ± 2°C
Relativna vlažnost zraka / *Relative Humidity of Air*:	47% ± 5%
Tlak / *Pressure*:	1017 ± 5 hPa

3.2 BAZNA OSJETLJIVOST / *BASE SENSITIVITY*

	Prije ugađanja / *Before adjustment*	Nakon ugađanja / *After adjustment*
BS	**4567,47**	**4509,69**

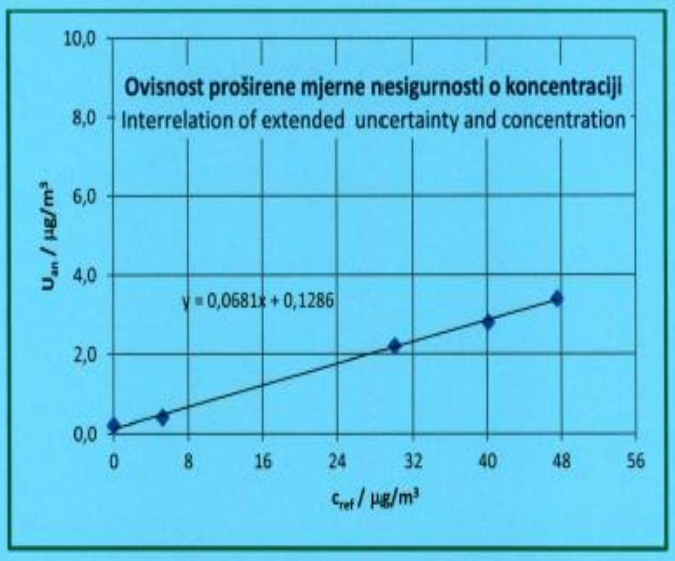
3.3 UGAĐANJE / *ADJUSTMENT*

Ugađanje analizatora provedeno je pri c(C_6H_6)= **40,1** µg/m^3 (**12,3** nmol/mol).
Adjustment of the analyzer is provided at c(C_6H_6)= **40,1** µg/m^3 (**12,3** nmol/mol).

3.4 REZULTATI UMJERAVANJA / *CALIBRATION RESULTS*

c,ref / µg/m^3	c,an / µg/m^3	Δc,an / µg/m^3	U,ref / µg/m^3	U,an / µg/m^3
0,0	0,0	0,0	0,0	0,2
5,2	5,0	-0,2	0,4	0,4
30,0	28,5	-1,5	2,1	2,2
40,1	38,6	-1,5	2,8	2,8
47,5	46,5	-1,0	3,3	3,4

c_{ref} – koncentracija referentnog plina / *reference gas concentration*
c_{an} – koncentracija plina koju pokazuje analizator / *gas concentration indicated by analyzer*
Δc – odstupanje analizatora / *deviation of the analyzer*
U_{ref} – proširena mjerna nesigumost umjeravanja referentnog plina / *expanded measurement uncertainty of reference gas*
U_{an} – proširena mjerna nesigumost analizatora / *expanded measurement uncertainty of analyzer*
***nmol/mol** uz usvojenu pretpostavku idealnog plina odgovara **ppbv**
**nmol/mol* *with the assumption of ideal gas corresponds to* ppbv



3.5 **PROVJERA RADNIH KARAKTERISTIKA** / *PERFORMANCE CHARACTERISTICS TESTS*

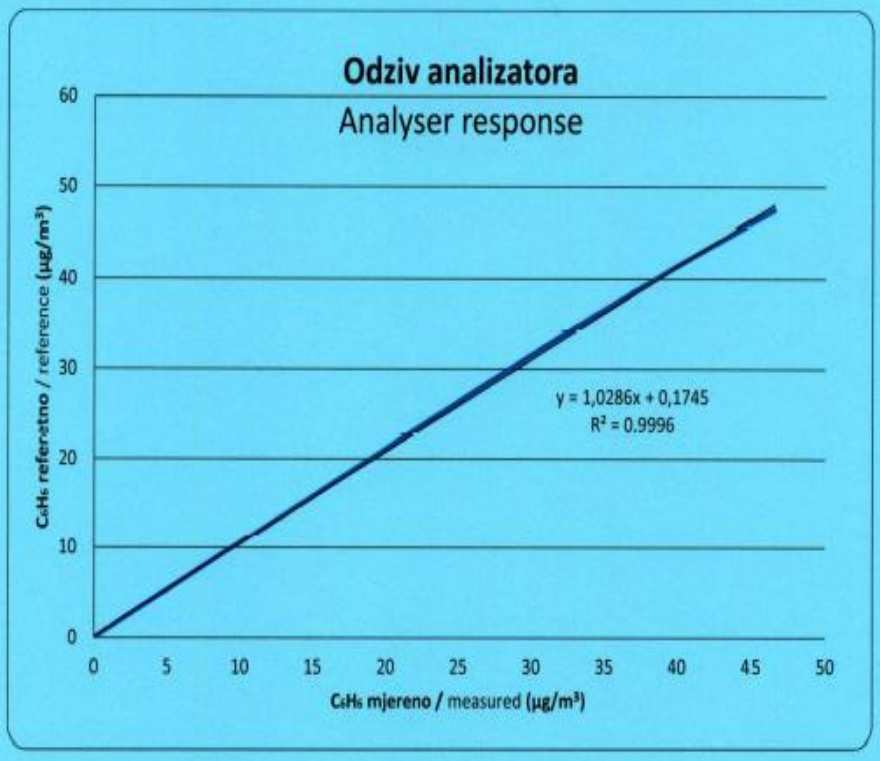
Broj prema Tablici 2 norme HRN EN 14662-3 Number according to Table 2 of the EN 14662-3	**Oznaka iz norme HRN EN 14662-3** Symbol according to EN 14662-3	**Karakteristika** Characteristic	**Rezultat provjere** (μm^{-3} ili %) Result of the check (μm^{-3} or %)	**Granice prihvatljivosti** Acceptance limits	**Sukladnost** Compliance
3	r_{LV}	**ponovljivost na graničnoj vrijednosti** repeatability at limit value	1,50%	r_{LV} < 5,0 %	Zadovoljava Complies
2	$r_{0,5}$	**ponovljivost na 1/10 GV (0,5 µg/m³)** repeatability at 0,5 µg/m³	0,05	$r_{0,5}$ < 0,3 μm^{-3}	Zadovoljava Complies
1	X_l	**nelinearnost, najveće odstupanje** lack of fit, largest residual	1,72%	< 5,0 %	Zadovoljava Complies
formula (33)	L	**granica detekcije** detection limit	0,05	N/A	
10	d_{24}	**kratkotrajni odmak na rasponu** short term drift at span value	0,50%	d_{24} < 5,0 %	Zadovoljava Complies

ZAKLJUČAK / *CONCLUSION*

Analizator **zadovoljava** granice prihvatljivosti definirane normom HRN EN 14662-3:2007.

*Analyzer **complies** with the acceptance limits according to EN 14662-3:2005.*

3.6 **ODZIV ANALIZATORA NAKON UGAĐANJA** / *THE ANALYZER RESPONSE AFTER ADJUSTMENT*



3.7 **MJERNA NESIGURNOST** / *MEASUREMENT UNCERTAINTY*

Izražena proširena mjerna nesigurnost umjeravanja prikazana je kao umnožak sastavljene mjerne nesigurnosti i faktora pokrivanja k=2, koji u slučaju normalne razdiobe odgovara približno 95%-tnoj vjerojatnosti pokrivanja. Sastavljena mjerna nesigurnost određena je u skladu s EA-4/02.

The reported expanded measurement uncertainty is stated as combined standard uncertainty multiplied by coverage factor k=2 which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard measurement uncertainty has been determinated in accordance with EA-4/02.

3.8 **NAPOMENA** / *NOTE*

Korisnik analizatora odgovoran je umjeravati ga u prikladnim vremenskim razmacima.

The user is obligated to have the analyzer recalibrated at appropriate intervals.

---------- *kraj potvrde o umjeravanju (end of calibration certificate)* ----------

EEA

Participating Laboratory	Executive Environment Agency, BULGARIA
Acronym	EEA
Person(s) responsible	Nikolay Panayotov
Contact e-mails:	npanayotov@abv.bg
Telephone contact:	00359 889 12 20 20

Characteristic of your BTEX analyser

Trademark	Environnement S.A.
Model:	VOC 72M
Version:	Benzene
Year of manufacture:	2013

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:	----	X	----	----	----
Other gases used:	----	----	----	----	----

Operating system:	Linux			
Cycle time, min:	15 min			
Adsorbent material:	Carbopack®			
Sampling control	Piston - Pump			
Sampling temperature, °C	35°C			
Sample volume, ml	165			
Number of adsorbent tubes	1			
Desorption temperature, `	380°C			
Desorption time, sec	60			
Desorption flow, ml/min	n/a			
Cryo-trap detail				
Trapping temperature, °C				
Desorption temperature, °C	380°C	Desorption time, sec	60	
Desorption flow, ml/min	15	split flow, ml/min		
Stripper column				
Analytical column				
phase:	n/a			
length, m:	15m			
diameter (ID) mm:	0.25mm			
thickness (µm):	1µm			
analytical conditions:	cold purge 0-10s at 25°C, injection 10-20s at 25°C,hot purge 20-30s at 25°C,trap cooling 30-80s at 25-30°C 5°C/min, trap sampling 80-900s 30-160°C 30°C/min			

Traceability of your calibration Standard

Certified reference material (CRM):	Calibration centre LAT №143, SIAD ITALY	
Certified by	Calibration centre LAT №143, SIAD ITALY	
Certified number:	307480 307491	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	10,00x10-9	0,60x10-9
Toluene	48,0x10-9	
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		
Other methods		
Dilution of CRM		
Static Injection		
Permeation		
Additional comments		

EEA

ФК 5.10 – 1

МИНИСТЕРСТВО НА ОКОЛНАТА СРЕДА И ВОДИТЕ

ИЗПЪЛНИТЕЛНА АГЕНЦИЯ ПО ОКОЛНА СРЕДА

1618 София, бул. " Цар Борис Ш " N136, ПК 251, ☎. 940 64 51, Факс : 955 90 15

КАЛИБРОВЪЧНА ЛАБОРАТОРИЯ – ИАОС

Акредитирана лаборатория за калибриране
Сертификат № 21 ЛК / Валиден до 20.01.2020 г.
Издаден от ИА БСА, съгласно БДС EN ISO/IEC 17025:2006

С Е Р Т И Ф И К А Т
З А
К А Л И Б Р И Р А Н Е
№ 115/26.08.2016г.

СРЕДСТВО ЗА ИЗМЕРВАНЕ: ГАЗАНАЛИЗАТОР ЗА БЕНЗЕН

ТИП (ОПИСАНИЕ): VOC72M

ПРОИЗВОДИТЕЛ: ENVIRONNEMENT S.A., ФРАНЦИЯ

ИДЕНТИФИКАЦИОНЕН НОМЕР: 57

НАИМЕНОВАНИЕ НА ЗАЯВИТЕЛЯ: ИАОС – КЛ

АДРЕС НА ЗАЯВИТЕЛЯ: 1618 СОФИЯ, БУЛ. "ЦАР БОРИС Ш" 136

МЯСТО НА ПРОВЕЖДАНЕ НА КАЛИБРИРАНЕТО: КЛ – ИАОС

Дата на калибриране: 25 – 26.08.2016г.

Сертификатът съдържа: 2 страници

Извършил калибрирането:

(инж. Вл. Георгиева)

Ръководител КЛ – ИАОС:

(инж. Н. Панайотов)

Сертификатът за калибриране без подпис на Ръководителя на КЛ – ИАОС и печат на лабораторията е невалиден. Сертификатът може да бъде възпроизвеждан само изцяло и с писменото разрешение на Ръководителя на КЛ ИАОС.

ФК 5.10 – 1

СИСТЕМАТА: ГАЗАНАЛИЗАТОР ЗА БЕНЗЕН се калибрира по методики за калибриране ВЛМ – ГА – 01 / 2015 и утвърдена от Ръководител КЛ – ИАОС.

МЕТОД ЗА КАЛИБРИРАНЕ:
Непосредствено сравнение на сертифицирани стойности на стандартните образци, използвани при калибрирането със стойностите на показанията на калибрираното средство за измерване.

УСЛОВИЯ ЗА КАЛИБРИРАНЕ:
температура на околната среда: 22.0 ^{0}C ± 0.06 ^{0}C;
атмосферно налягане: 952 hPa ± 1.0 hPa;
относителна влажност на въздуха: 21 %RH ± 1.5 %

МЕТРОЛОГИЧНА ПРОСЛЕДИМОСТ:
Калибрирането е извършено със сравнителни материали за състав на газ със сертифицирани метрологични характеристики.

№ по ред	Сравнителен материал	Сертифицирана стойност /ppb/	Отн. U неопределеност,%	Идентификация, производител
1	C6H6	5.1	6.0	№ 307479/04.09.2016г. SIAD № W044915 LAT№143 LAT/025
2	C6H6	15.01	6.0	№ 307486/04.09.2016г. SIAD № W045115 LAT№143 LAT/025
3	C6H6	48.0	6.0	№ 307491/04.09.2016г. SIAD № W045215 LAT№143 LAT/025

РЕЗУЛТАТИ ОТ КАЛИБРИРАНЕТО :

1. C6H6

Обхват на калибриране	Стойност на ССМ /ppb/	Измерена стойност /ppb/	Неопределеност на измерването U, /ppb/
от 0.16 ppb до 50 ppb	5.10	4.84	0.31
от 0.16 ppb до 50 ppb	15.01	15.24	0.90
от 0.16 ppb до 50 ppb	48.0	46.98	2.88

НЕОПРЕДЕЛЕНОСТ НА ИЗМЕРВАНЕТО:
Разширената неопределеност от измерване при калибрирането е изразена като комбинирана стандартна неопределеност от измерване, умножена по множител на покритие k = 2, което за нормално разпределение съответства на доверителна вероятност около 95%. Неопределеност на измерването при калибриране се определя в съответствие с изискванията на документ EA – 04/02M:2013 "Оценка на неопределеността от измерване при калибриране".

Извършил калибрирането:

(инж. Вл. Георгиева)

VMM-1

Participating Laboratory	Vlaamse Milieumaatschappij
Acronym	VMM
Person(s) responsible	Sarah Decoux, Jan Petré
Contact e-mails:	s.decoux@vmm.be + j.petre@vmm.be
Telephone contact:	Sarah Decoux: +323 216 61 09 / +32470 19 10 96, Jan Petré: +323 216 61 08 /

Characteristic of your BTEX analyser

Trademark	Synspec
Model:	GC 955-601
Version:	GC 955
Year of manufacture:	2013

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		x			
Other gases used:					x

Operating system:	Windows XP			
Cycle time, min:	15 min.			
Adsorbent material:	Tenax GR			
Sampling control	piston/pump			
Sampling temperature, °C	ambient temperature			
Sample volume, ml	140 ml			
Number of adsorbent tubes	1			
Desorption temperature, `	180°C			
Desorption time, sec	60 sec			
Desorption flow, ml/min	1,5 ml/min			
Cryo-trap detail				
Trapping temperature, °C				
Desorption temperature, °C		Desorption time, sec		
Desorption flow, ml/min		split flow, ml/min		
Stripper column	capillary column (2m)			
Analytical column	capillary column			
phase:	95% dimethylpolysiloxane + 5% diphenylpolysiloxane			
length, m:	13 m			
diameter (ID) mm:	0,32 mm			
thickness (µm):	1 µm			
analytical conditions:	50°C (3 min) --> 70°C (7 min (2°/min))			

Traceability of your calibration Standard

Certified reference material (CRM):	system MFCair 10 sl/min, MFCbtex 100 sml/min) from certified high concentra
Certified by	VMM-lab: certified standard and dilution system
Certified number:	

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	5.029	
Toluene	5.088	
Ethyl-benzene	4.8	
m-Xylene	5.048	
p-Xylene	4.86	
o-Xylene	5.088	

Other methods	
Dilution of CRM	AirQrate, 400 ppb dillution system
Static Injection	
Permeation	
Additional comments	

VMM-2

Participating Laboratory	Vlaamse Milieumaatschappij
Acronym	VMM
Person(s) responsible	Sarah Decoux, Jan Petré
Contact e-mails:	s.decoux@vmm.be + j.petre@vmm.be
Telephone contact:	Sarah Decoux: +323 216 61 09 / +32470 19 10 96, Jan Petré: +323 216 61 08 / +32474 92 08 16

Characteristic of your BTEX analyser

Trademark	Chromatotec group
Model:	GC 866
Version:	A31022
Year of manufacture:	2011

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:			x		
Other gases used:					x

Operating system:	Windows embedded (software Vistachrom 1.47)		
Cycle time, min:	15 min.		
Adsorbent material:	Carbotrap		
Sampling control	pump/critical orifice 76 µm		
Sampling temperature, °C	Ambient temperature		
Sample volume, ml	+/- 450 ml		
Number of adsorbent tubes	1		
Desorption temperature, `	380°C		
Desorption time, sec	120 sec.		
Desorption flow, ml/min	3-4 ml/min.		
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column			
Analytical column	MXT 30 CE (metallic column)		
phase:			
length, m:	30 m		
diameter (ID) mm:	0,28 mm		
thickness (µm):	1 µm		
analytical conditions:	--> 45°C (60 sec (2°)) --> 165°C (480 sec (15°)) --> 165°C (120 sec(0°)) --> 43°C --> ...		

Traceability of your calibration Standard

Certified reference material (CRM):	system MFCair 10 sl/min, MFCbtex 100 sml/min) from certified high concentra	
Certified by	VMM-lab: certified standard and dilution system	
Certified number:		
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	5.029	
Toluene	5.088	
Ethyl-benzene	4.8	
m-Xylene	5.048	
p-Xylene	4.86	
o-Xylene	5.088	
Other methods		
Dilution of CRM	AirQrate, 400 ppb dillution system	
Static Injection		
Permeation		
Additional comments		

VMM

BTEX - monitor Synspec : Formulier voor de standaardcontrole en kalibratie FdBDV-xxx-1 uitgave 1 - 01/04/2014

Nummer station : -999, Plaats : , Inventarisnummer : LM00292

Datum: 20/09/16 van 07:00 UT tot 11:50 UT

Naam: SDE

☐ preventief: ☐ 2-maandelijk ☐ 6-maandelijks ☐ jaarlijks

☐ correctief: Objectnummer:

☒ op aanvraag:

Instellingen

☒ Opstelling in overeenstemming met BDV-xxx	☐ Opstelling niet in overeenstemming met BDV-xxx
☒ Instelling in overeenstemming met BDV-xxx	☐ Instelling niet in overeenstemming met BDV-xxx

Controle parameters in PC

Sample press:	845	mbar (700-1050	Oventemp:	68	°C (50-70°C)
Sample count:	960	(0-1000)	Ambient:	29.0	°C
Pressure:	3.7	bar	foutmeldingen op scherm?		nee
Flow:	1.4	ccm	Retention time lock PID op scherm?		ja

Kalibratie BTEX-monitor mbv ijkvalies (3 concentratieniveaus)

- Concentratie ~2 ppb: verdunningsdebiet ijkvalies = ml/min

- Kalibratieanalysen: = ml/min

	theor. conc	tijd (uu:mm) 10:30			tijd (uu:mm) 10:45			tijd (uu:mm) 11:00			%
	(µg/m³)	RT	opp	conc	RT	opp	conc	RT	opp	conc	
benzeen	6.734	251.0	141465	6.590		142949	6.660		142219	6.630	1.6
tolueen	6.672	374.0	167845	6.430		170425	6.530		170067	6.520	2.7
ethbenzeen	6.638	580.0	182507	6.340		182818	6.350		179866	6.250	4.9
m+p-xyleen	13.105	604.0	356980	12.200		360208	12.310		358495	12.260	6.5
o-xyleen	6.814	685.0	185139	6.330		159836	6.390		156836	6.270	7.1

- Concentratie ~3 ppb: verdunningsdebiet ijkvalies = ml/min

- Kalibratieanalysen: = ml/min

	theor. conc	tijd (uu:mm) 11:30			tijd (uu:mm) 11:45			tijd (uu:mm) 12:00			%
	(µg/m³)	RT	opp	conc	RT	opp	conc	RT	opp	conc	
benzeen	4.768	251.0	106494	4.960		106184	4.950		104428	4.870	3.3
tolueen	4.711	375.0	128088	4.910		131161	5.030		125879	4.820	4.4
ethbenzeen	4.572	580.0	140231	4.870		141076	4.900		140995	4.900	7.0
m+p-xyleen	8.713	605.0	281696	9.630		284329	9.720		278749	9.590	10.7
o-xyleen	4.256	685.0	122044	4.880		122840	4.910		122191	4.890	15.0

- Concentratie ~5 ppb: verdunningsdebiet ijkvalies = ml/min

- Kalibratieanalysen: = ml/min

	theor. conc	tijd (uu:mm) 12:45			tijd (uu:mm) 13:00			tijd (uu:mm) 13:15			%
	(µg/m³)	RT	opp	conc	RT	opp	conc	RT	opp	conc	
benzeen	1.284	252.0	32547	1.520		31494	1.470		31592	1.470	15.8
tolueen	1.166	375.0	42023	1.610		39346	1.510		39280	1.500	32.1
ethbenzeen	1.077	581.0	49503	1.720		45722	1.590		44902	1.560	50.7
m+p-xyleen	2.038	605.0	115435	3.950		102363	3.500		98318	3.360	76.8
o-xyleen	0.964	686.0	45312	1.810		38107	1.520		37849	1.510	67.4

VMM

Aanpassingen van responsfactoren (RF) en referentietijden (RT)

☐ RF zijn binnen de grenzen	☐ RF zijn niet binnen de grenzen
☐ RT zijn binnen de grenzen	☒ RT zijn niet binnen de grenzen

	oude RF	nieuwe RF	oude RT (min-max)		nieuwe RT (min-max)	
benzeen	0.0000502	0.0000466			241	261
tolueen	0.0000393	0.0000383			364	484
ethbenzeen	0.000035	0.0000348			568	592
m+p-xyleen	0.0000345	0.0000342			591	620
o-xyleen	0.0000426	0.00004			673	693

Opmerkingen: Ispra ijking op 7 en 5 en 1.4 ppb.

VMM

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS REFERENCE MATERIALS 4002

PRIMARY REFERENCE GAS MIXTURE

Cylinder Number: D38 6683

CUSTOMER: **Flanders Environment Agency (VMM)**

ADDRESS: Vlaamse Milieumaatschappij, Afdeling Lucht, Milieu en Communicatie, Kronenburgstraat 45 bus B3, 2000 Antwerpen, Belgium

CALIBRATION DATE: 21-28 April 2016

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)		
1,2-dichloroethane*	198	±	10
Benzene	196.5	±	3.9
Toluene	196.6	±	4.9
Ethylbenzene	195.9	±	4.9
m-xylene + *p*-xylene	199	±	5
o-xylene	199	±	5
Nitrogen	Balance		

*denotes component outside ISO Guide 34 but within ISO 17025

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue
NPL cannot guarantee the stability of 1,2-dichloroethane

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2016010309 **Date of issue:** 29 April 2016

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

NPLC04-0813

EPA

Participating Laboratory	EPA Ireland				
Acronym	EPA				
Person(s) responsible	Patrick Malone, Micheál O'Dwyer				
Contact e-mails:	p.malone@epa.ie, m.odwyer@epa.ie				
Telephone contact:	35312680154				
Characteristic of your BTEX analyser					
Trademark	Syntech				
Model:	Syntech GC955				
Version:	600				
Year of manufacture:	2008				
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		yes			
Other gases used:					
Operating system:	Windows XP				
Cycle time, min:	15 min				
Adsorbent material:	Tenax GR 35/60				
Sampling control	sample pump/piston pump				
Sampling temperature, °C	Ambient				
Sample volume, ml	210				
Number of adsorbent tubes	1				
Desorption temperature, `	180				
Desorption time, sec	60				
Desorption flow, ml/min	1.5				
Cryo-trap detail	n/a				
Trapping temperature, °C					
Desorption temperature, °C		Desorption time, sec			
Desorption flow, ml/min		split flow, ml/min			
Stripper column	Length 2m. Same as the analytical column.				
Analytical column	Altech - p/n:13710, AT-5				
phase:	(5% Phenyl)-95% Methylpolysiloxane				
length, m:	13				
diameter (ID) mm:	0.32				
thickness (µm):	1.0				
analytical conditions:	Initial Temp of 45°C, hold for 4 mins. Ramp to 80°C over the next 6.5mins. Hold at 80°C for 1 min. Return to 45°C.				
Traceability of your calibration Standard					
Certified reference material (CRM):	Gas Mixture				
Certified by	NPL				
Certified number:	2015080135				
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)			
Benzene	10.11 ppb	±0.2			
Toluene	10.24 ppb	±0.26			
Ethyl-benzene	9.67 ppb	±0.25			
m-Xylene and p-Xylene	19.93 ppb	±0.5			
p-Xylene					
o-Xylene	10.23 ppb +/- 0.26	±0.26			
Other methods					
Dilution of CRM					
Static Injection					
Permeation					
Additional comments					

EPA

NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS REFERENCE MATERIALS 4002

PRIMARY REFERENCE GAS MIXTURE

Cylinder Number: D38 6627

CUSTOMER: **Environmental Protection Agency**
ADDRESS: Seville Lodge, Callan Road, Kilkenny, R95 ED28, Ireland
CALIBRATION DATE: 23 September 2015

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Benzene	10.11 ± 0.20
Toluene	10.24 ± 0.26
Ethylbenzene	9.67 ± 0.25
m-xylene + *p*-xylene	19.93 ± 0.50
o-xylene	10.23 ± 0.26
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)
TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards
EXPIRY: Certificate valid for 2 years from the date of issue
PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar
STORAGE: No special precautions are required
HANDLING: Refer to ISO 16664
OUTLET: DIN 477 No. 1 valve
INTENDED USE: Calibration standard

Reference: 2015080135 **Date of issue:** 25 September 2015
Signed: (Authorised Signatory)
Name: Dr P J Brewer (on behalf of NPLML)
Checked by:

Participating Laboratory	Ricardo Energy and Environment	**REE**
Acronym	REE	
Person(s) responsible	James Dernie / Pedro Abreu	
Contact e-mails:	james.dernie@ricardo.com and pedro.abreu@ricardo.com	
Telephone contact:	0044 1235 753643 and 0044 1235 753707	

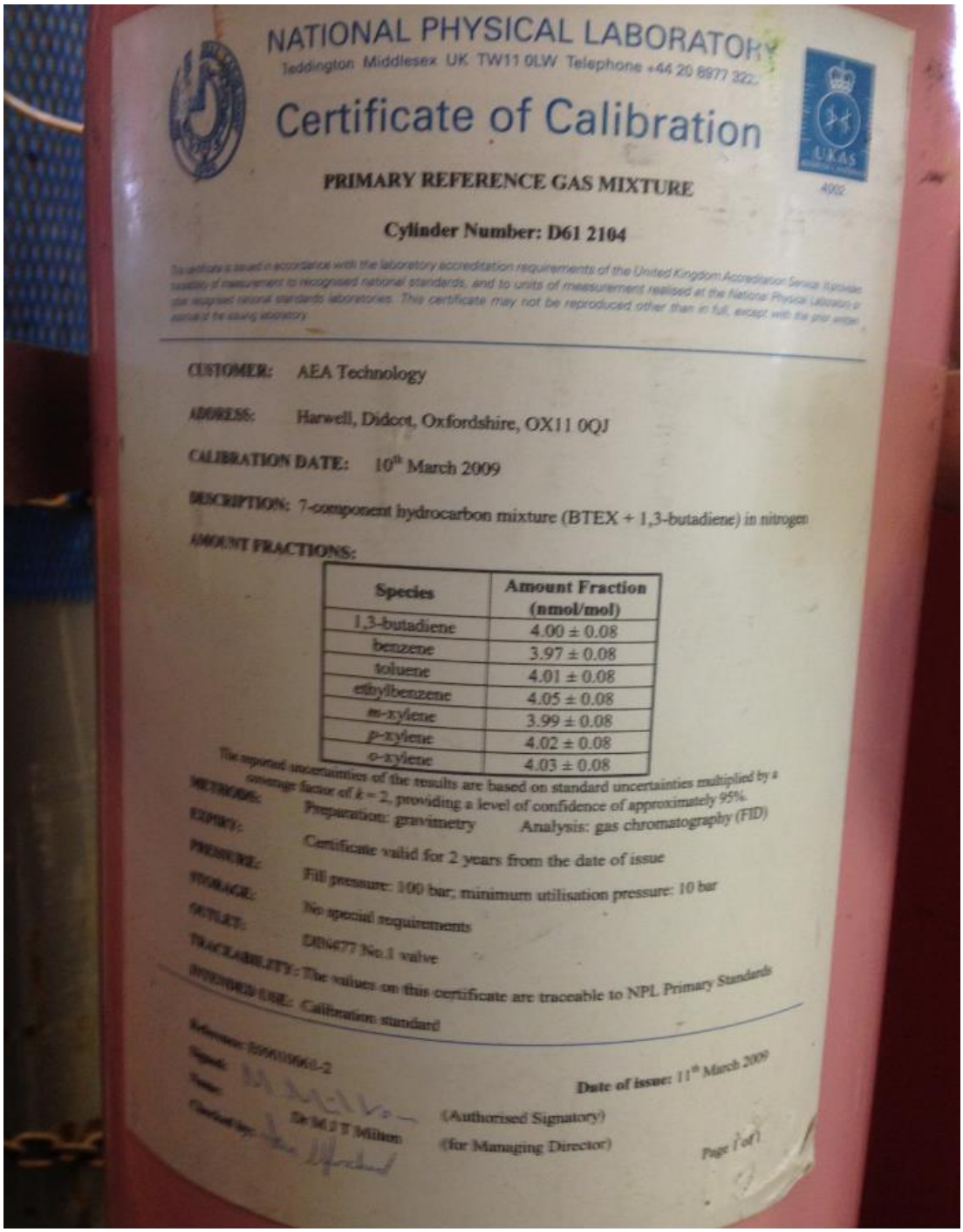
Characteristic of your BTEX analyser

Trademark					
Model:	Environnement S.A VOC71				
Version:	PID-13BDIENE Version				
Year of manufacture:	2001				
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		✓			
Other gases used:					
Operating system:	Windows				
Cycle time, min:	15				
Adsorbent material:	Carbotrap/carbopack				
Sampling control	pump/critical orifice				
Sampling temperature, °C	Ambient temperature				
Sample volume, ml	900				
Number of adsorbent tubes	2				
Desorption temperature, `	340				
Desorption time, sec	180				
Desorption flow, ml/min	1				
Cryo-trap detail	carbopack B				
Trapping temperature, °C	Ambient temperature				
Desorption temperature, °C	as above	Desorption time, sec	as above		
Desorption flow, ml/min	as above	split flow, ml/min	as above		
Stripper column	N/A				
Analytical column	Supelco SPB624				
phase:	propietry, bonded				
length, m:	13				
diameter (ID) mm:	0.32				
thickness (µm):	1.8				
analytical conditions:	34 c for 115 seconds, ramp of 20 c per min for 260 seconds. 150 c for 155 seconds				

Traceability of your calibration Standard

Certified reference material (CRM):	Secondary gas standard prepared by NPL	
Certified by	NPL	
Certified number:	D61 2104	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	3.97	0.08
Toluene	4.01	0.08
Ethyl-benzene	4.05	0.08
m-Xylene	3.99	0.08
p-Xylene	4.02	0.08
o-Xylene	4.03	0.08
Other methods		
Dilution of CRM	NA	
Static Injection	Using a cylinder (d61 2104) with excess flow and metering valve	
Permeation	Using a cylinder	
Additional comments		

REE



NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 322..

Certificate of Calibration

PRIMARY REFERENCE GAS MIXTURE

4002

Cylinder Number: D61 2104

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: AEA Technology

ADDRESS: Harwell, Didcot, Oxfordshire, OX11 0QJ

CALIBRATION DATE: 10th March 2009

DESCRIPTION: 7-component hydrocarbon mixture (BTEX + 1,3-butadiene) in nitrogen

AMOUNT FRACTIONS:

Species	Amount Fraction (nmol/mol)
1,3-butadiene	4.00 ± 0.08
benzene	3.97 ± 0.08
toluene	4.01 ± 0.08
ethylbenzene	4.05 ± 0.08
m-xylene	3.99 ± 0.08
p-xylene	4.02 ± 0.08
o-xylene	4.03 ± 0.08

The reported uncertainties of the results are based on standard uncertainties multiplied by a coverage factor of $k = 2$, providing a level of confidence of approximately 95%.

METHODS: Preparation: gravimetry Analysis: gas chromatography (FID)

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; minimum utilisation pressure: 10 bar

STORAGE: No special requirements

OUTLET: DIN477 No.1 valve

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

INTENDED USE: Calibration standard

Reference: 8990109661-2

Signed: (Authorised Signatory)

Name: Dr M J T Milton (for Managing Director)

Checked by:

Date of issue: 11th March 2009

Page 1 of 1

LIKZ

Participating Laboratory	Ambient air testing laboratory, Croatian Hydrological and Meteorological Service
Acronym	LIKZ
Person(s) responsible	Lovro Hrust, Lukša Kraljević
Contact e-mails:	lovro.hrust@cirus.dhz.hr
Telephone contact:	+3854565683, +385981932404

Characteristic of your BTEX analyser

Trademark	Syntech spectras
Model:	GC955
Version:	601
Year of manufacture:	2013

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		×			
Other gases used:					

Operating system:	Windows XP Embeded			
Cycle time, min:	15			
Adsorbent material:	Tenax GR			
Sampling control	pump/MFC , piston			
Sampling temperature, °C	5 - 35			
Sample volume, ml	93			
Number of adsorbent tubes	1			
Desorption temperature, `	180 °C			
Desorption time, sec	appx. 1 min			
Desorption flow, ml/min	n/a			
Cryo-trap detail	—			
Trapping temperature, °C	Ambient temperature			
Desorption temperature, °C	—	Desorption time, sec	—	
Desorption flow, ml/min	—	split flow, ml/min	—	
Stripper column	solid, capillary column type, 2m			
Analytical column	CP 70003 (Synspec SY-1) - 100% Dimethylpolysiloxane			
phase:	solid, capillary column type			
length, m:	13			
diameter (ID) mm:	n/a			
thickness (µm):	n/a			
analytical conditions:	50 °C (3min), 50°-> 70°C (2min), 70°C (7 min), 70°C->50°C(2min), 50°C(1min)			

Traceability of your calibration Standard

Certified reference material (CRM):	NPL BTEX gas mixture	
Certified by	NPL	
Certified number:	2015050241	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	100.9	2.0
Toluene	102.2	2.7
Ethyl-benzene	96.4	2.4
m-Xylene	198.9	9.9
p-Xylene		
o-Xylene	102.1	2.7

Other methods	
Dilution of CRM	1:10 – 1:1000, Teledyne API T700
Static Injection	two mass flow controllers, one for source gas and one for diluent
Permeation	
Additional comments	

LIKZ

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS REFERENCE MATERIALS 4002

PRIMARY REFERENCE GAS MIXTURE

Cylinder Number: D31 6721

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: **Meteorological and Hydrological Service**

ADDRESS: Gric 3, Zagreb, Croatia

CALIBRATION DATE: 28 August 2015

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Benzene	100.9 ± 2.0
Toluene	102.2 ± 2.6
Ethylbenzene	96.4 ± 2.5
m-xylene + *p*-xylene	198.9 ± 5.0
o-xylene	102.1 ± 2.6
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2015050241 **Date of issue:** 03 September 2015

Signed: (Authorised Signatory)

Name: Dr R J C Brown (on behalf of NPLML)

Checked by:

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognise the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

AAA

Participating Laboratory	Environmental Protection Agency (Lithuania)
Acronym	EPA
Person(s) responsible	Juozas Molis, Tomas Gaižutis
Contact e-mails:	j.molis@aaa.am.lt, t.gaizutis@aaa.am.lt
Telephone contact:	. Molis +370 706 62036 (work), +370 686 17501 (mob), T.Gaizutis +370 706 63471 (work

Characteristic of your BTEX analyser

Trademark	AMA Instruments
Model:	GC 5000 BTX FID
Version:	3
Year of manufacture:	2011

	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:		x			
Other gases used:			x		x

Operating system:	Windows XP Professional		
Cycle time, min:	30		
Adsorbent material:	Carbotrap		
Sampling control	MFC		
Sampling temperature,°C	30		
Sample volume, ml	300		
Number of adsorbent tubes	1		
Desorption temperature, `	230 °C		
Desorption time, sec	180		
Desorption flow, ml/min	2		
Cryo-trap detail	none		
Trapping temperature, °C	Ambient temperature		
Desorption temperature, °C		Desorption time, se	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	none		
Analytical column			
phase:	AMAsep 1		
length, m:	30		
diameter (ID) mm:	0.32		
thickness (µm):	1.5		
analytical conditions:	50°C (3min), 8°C/min, 130°C (5min)		

Traceability of your calibration Standard

Certified reference material (CRM):	Calibrated Gas Mixture	
Certified by	National Physical Laboratory (UK)	
Certified number:		
Compound	oncentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	4990	100
Toluene	5110	100
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		
Other methods		
Dilution of CRM	dilution factor: 500, Dilutor: Umwelttechnik MCZ GmbH	
Static Injection		
Permeation	Benzene 15ng/min, temperature: 50°C, Horiba GmbH	
Additional comments		

AAA

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS CALIBRATION 0478

CALIBRATED GAS MIXTURE

Cylinder Number: P2565L1545A

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provide traceability of measurement to recognised national standards, and to units of measurement realised at the National Physical Laboratory other recognised national standards laboratories. This certificate may not be reproduced other than in full, except with the prior writte approval of the issuing laboratory.

CUSTOMER: CryoService Limited

ADDRESS: Prescott Drive, Warndon Business Park, Worcester WR4 9RH

CALIBRATION DATE: 16th December 2009

CERTIFIED AMOUNT FRACTION:

Species	Amount Fraction µmol/mol
Benzene	(4.99 ± 0.1)
Toluene	(5.11 ± 0.1)
Nitrogen	Balance

The reported uncertainty of the result is based on the standard uncertainty multiplied by a coverage factor of $k = 2$, providing a level of confidence of approximately 95%.

METHODS: Analysis: Gas Chromatography (FID)

EXPIRY: Not applicable

PRESSURE: Minimum utilisation pressure: 10 bar

STORAGE: No special requirements

OUTLET: BS 341 No 3 valve.

TRACEABILITY: The value on this certificate is traceable to NPL Primary Standards.

Reference: 2009080106-2 **Date of issue:** 16th December 2009

Signed: M Milton (Authorised Signatory)

Name: Dr M J T Milton (for Managing Director)

Checked by:

Page 1 of 1

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

CHMI

Participating Laboratory	Czech Hydrometeorological Institute - Calibration Laboratory of Immission					
Acronym	CHMI - CLI					
Person(s) responsible	Ing. Miroslav Vokoun					
Contact e-mails:	vokoun@chmi.cz					
Telephone contact:	+420 24403 3458, +420 24403 3442					
Characteristic of your BTEX analyser						
Trademark	Environnement, S.A.					
Model:	VOC71M-PID					
Version:	VOC71M-PID with Micro III board					
Year of manufacture:	2005					
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air	
Carrier gas:		yes				
Other gases used:					yes	
Operating system:	Environnement, S.A. 1M series					
Cycle time, min:	15					
Adsorbent material:	Carbotrap, Carbopack B					
Sampling control						
Sampling temperature, °C	Ambient temperature					
Sample volume, ml	70 ml/min					
Number of adsorbent tubes	1					
Desorption temperature, `	350					
Desorption time, sec	180					
Desorption flow, ml/min	40					
Cryo-trap detail						
Trapping temperature, °C	Ambient temperature					
Desorption temperature, °C	350	Desorption time, sec	180			
Desorption flow, ml/min	40	split flow, ml/min				
Stripper column						
Analytical column	EPA 624					
phase:						
length, m:	10					
diameter (ID) mm:						
thickness (µm):						
analytical conditions:	0"÷120" 42°C, 120"÷185" 45°C, 185"÷545" ramp to 150°C, 545"÷740" 150°C					
Traceability of your calibration Standard						
Certified reference material (CRM):	PRM NPL 30HCs species in N2					
Certified by	NPL					
Certified number:	D86 0586					
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)				
Benzene	10.10	0.20				
Toluene	10.10	0.25				
Ethyl-benzene	9.81	0.25				
m+p-Xylene	19.87	0.50				
o-Xylene	10.06	0.25				
Other methods						
Dilution of CRM	Dilution PRM D86 0586 by static manometric injection					
Static Injection	Static manometric injection PRM by N2 to canister Silcosteel 6 l					
Permeation						
Additional comments						
linearity test: Horiba ASGU-340 - HA-0212						

CHMI

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

PRIMARY REFERENCE GAS MIXTURE

UKAS 4002

Cylinder Number: D86 0586

RECERTIFICATION

Previous Reference: 2012020211, dated May 2012

CUSTOMER: **Czech Hydrometeorological Institute**

ADDRESS: Calibration Laboratory of Immission, Generala Sisky 942/1, 143 00 Prague 4, Czech Republic

CALIBRATION DATE: 5 August 2014

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)	Component	Amount fraction / (nmol/mol)
Ethane	10.09 ± 0.20	2-methylpentane	10.13 ± 0.20
Ethene	9.73 ± 0.19	Hexane	9.94 ± 0.20
Propane	10.19 ± 0.20	Isoprene	10.03 ± 0.20
Propene	**10.01 ± 0.20**	**Heptane**	**10.02 ± 0.20**
2-methylpropane	10.48 ± 0.26	Benzene	10.10 ± 0.20
Butane	9.91 ± 0.20	2,2,4-trimethylpentane	9.94 ± 0.20
Ethyne	10.23 ± 0.51	Octane	10.05 ± 0.20
trans-but-2-ene	9.89 ± 0.20	Toluene	10.10 ± 0.25
But-1-ene	9.91 ± 0.20	Ethylbenzene	9.81 ± 0.25
cis-but-2-ene	10.03 ± 0.20	*m*-xylene + *p*-xylene	19.87 ± 0.50
2-methylbutane	10.08 ± 0.20	*o*-xylene	10.06 ± 0.25
Pentane	10.08 ± 0.20	1,3,5-trimethylbenzene	10.06 ± 0.25
1,3-butadiene	9.88 ± 0.20	1,2,4-trimethylbenzene	10.23 ± 0.26
trans-pent-2-ene	9.89 ± 0.20	1,2,3-trimethylbenzene	9.71 ± 0.24
Pent-1-ene	9.91 ± 0.20	Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Pressure at recertification: 65 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No.1 valve

INTENDED USE: Calibration standard

Reference: 2014030346 **Date of issue:** 13 August 2014

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

LCSQA

Participating Laboratory	Mines Douai - Dpt SAGE				
Acronym	SAGE- MD				
Person(s) responsible	Nadine LOCOGE				
Contact e-mails:	nadine.locoge@mines-douai.fr / thierry.leonardis@mines-douai.fr				
Telephone contact:	+ 333 27 71 26 19 / + 333 27 71 26 27				
Characteristic of your BTEX analyser					
Trademark	CHROMATOTEC				
Model:	VOC C6-C12				
Version:					
Year of manufacture:	2008				
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air
Carrier gas:	---	---	YES	---	---
Other gases used:	---	---	YES	---	YES
Operating system:	VISTACHROM				
Cycle time, min:	30 min				
Adsorbent material:	Carbo trap				
Sampling control	Critical Orifice_ electronic flow measurement				
Sampling temperature, °C	Ambient temperature				
Sample volume, ml	920				
Number of adsorbent tubes	1				
Desorption temperature, `					
Desorption time, sec					
Desorption flow, ml/min					
Cryo-trap detail					
Trapping temperature, °C	Ambient temperature				
Desorption temperature, °C	380	Desorption time, sec	240		
Desorption flow, ml/min	3.5	split flow, ml/min	no split		
Stripper column					
Analytical column	metallic capillary column				
phase:	apolar and special Chromatotec condtionning				
length, m:	30				
diameter (ID) mm:	0.28				
thickness (µm):	1				
analytical conditions:	initial temp : 36°C -1 - 6 min : ramp at 2°C/min (inj at t=0, 38°C) 6min-9min : ramp at 10°C/min 9min-17min : ramp at 15°C/min 200°C during 240sec.				
Traceability of your calibration Standard					
Certified reference material (CRM):					
Certified by					
Certified number:					
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)			
Benzene					
Toluene					
Ethyl-benzene					
m-Xylene					
p-Xylene					
o-Xylene					
Other methods					
Dilution of CRM					
Static Injection					
Permeation					
Additional comments					

LCSQA

LABORATOIRES DE PARIS
1, rue Gaston Boissier - 75724 Paris Cedex 15
Tél. : 01 40 43 37 00 - Fax : 01 40 43 37 37

Commande : Convention LNE/LCSQA

CERTIFICAT D'ETALONNAGE

N° P151864 / 272

Délivré à : **MINES DOUAI**
Département Chimie et Environnement
941, rue Charles Bourseul
59508 DOUAI Cedex

INSTRUMENT ETALONNE

Désignation : **Bouteille contenant un mélange gazeux de benzène, toluène, éthylbenzène, p-xylène, m-xylène et o-xylène dans l'azote.**

Constructeur : **Messer**

Type : **B20** N° d'identification : **620064**

Ce certificat comprend **4 pages** Date d'émission : **8 septembre 2016**

Le Responsable de l'étalonnage

Christophe SUTOUR

Accréditation
N° 2-54
Portée disponible sur www.cofrac.fr

1. DESIGNATION

- Bouteille contenant un mélange gazeux de benzène, toluène, éthylbenzène, p-xylène, m-xylène et o-xylène dans l'azote.

- Type de bouteille	: B20
- Fabricant	: Messer
- N° d'identification	: 620064
- Pression avant étalonnage	: 180 bars
- Pression après étalonnage	: 175 bars

Composé	Concentration du fabricant (nmol/mol)	Incertitude du fabricant (nmol/mol)
Benzène	15,0	10 %
Toluène	15,0	10 %
Ethylbenzène	15,0	10 %
p-xylène	15,0	10 %
m-xylène	15,0	10 %
o-xylène	15,0	10 %

2. CONDITIONS D'ETALONNAGE

2.1. MELANGE GAZEUX ETALON

Le mélange gazeux étalon est obtenu par dilution dynamique de mélanges gazeux de référence gravimétriques haute concentration fabriqués au LNE.

Composé	Identification du mélange de référence gravimétrique utilisé pour l'étalonnage de la bouteille n° 620064
Benzène	BEN/N2 0036
Toluène	TOL/N2 0028
Ethylbenzène	EBEN/N2 0015
p,m,o-xylène	OMP-X/N2 0008

2.2. INSTRUMENTS UTILISES

- Salle climatisée 21 °C ± 2 °C
- Débitmètres MOLBLOC 5 l/min et 100 ml/min à 273,15 K et à 1013,25 hPa
- Chromatographe INTERSCIENCE Compact GC (CHR 0023)
- Le manodétendeur livré avec la bouteille n'a pas été utilisé pour réaliser l'étalonnage.

suite du certificat page suivante

2.3. METHODE DE MESURE

L'analyse du mélange gazeux est effectuée par chromatographie en phase gazeuse avec détection à ionisation de flamme selon le mode opératoire suivant :

- ✓ Analyse du mélange gazeux à titrer ;
- ✓ Analyse du mélange gazeux étalon ;
- ✓ Analyse du gaz de dilution.

Les concentrations des composés analysés pour le mélange gazeux sont calculées à partir des surfaces des pics obtenus pour le mélange gazeux à titrer, le mélange gazeux étalon et le gaz de dilution et de la concentration du mélange gazeux étalon.

3. RESULTATS

Le résultat de l'étalonnage est reporté dans le tableau ci-après.

Etalonnage réalisé par :	**Laurent SARAGOZA**
Etalonnage réalisé le :	**06/09/2016**
N° d'identification :	**620064**

Constituant	Concentration mesurée (en nmol/mol)	Incertitude élargie (en nmol/mol)
Benzène	14,00	0,16
Toluène	13,53	0,16
Ethylbenzène	12,92	0,16
p-xylène	13,69	0,20
m-xylène	13,82	0,20
o-xylène	13,26	0,19

suite du certificat page suivante

4. INCERTITUDES

Les incertitudes élargies mentionnées sont celles correspondant à deux fois l'incertitude-type composée. Les incertitudes-types ont été calculées en tenant compte des différentes sources d'incertitudes, étalons de référence, moyens d'étalonnage, conditions d'environnement, contribution de l'instrument étalonné, répétabilité...

Ce certificat d'étalonnage garantit le raccordement des résultats d'étalonnage au Système International d'unités (SI).

fin du certificat d'étalonnage

LCSQA

LNE
Le progrès, une passion à partager

LABORATOIRES DE PARIS
1, rue Gaston Boissier - 75724 Paris Cedex 15
Tél. : 01 40 43 37 00 - Fax : 01 40 43 37 37

Commande : Convention LNE/LCSQA

CERTIFICAT D'ETALONNAGE

N° P151864 / 272

Délivré à : **MINES DOUAI**
Département Chimie et Environnement
941, rue Charles Bourseul
59508 DOUAI Cedex

INSTRUMENT ETALONNE

Désignation : **Bouteille contenant un mélange gazeux de benzène, toluène, éthylbenzène, p-xylène, m-xylène et o-xylène dans l'azote.**

Constructeur : **Messer**

Type : **B20** N° d'identification : **620064**

Ce certificat comprend **4 pages** Date d'émission : **8 septembre 2016**

Le Responsable de l'étalonnage

Christophe SUTOUR

cofrac
ETALONNAGE

Accréditation
N° 2.54
Portée disponible sur www.cofrac.fr

LCSQA

1. DESIGNATION

- Bouteille contenant un mélange gazeux de benzène, toluène, éthylbenzène, p-xylène, m-xylène et o-xylène dans l'azote.

- Type de bouteille	: B20
- Fabricant	: Messer
- N° d'identification	: 620064
- Pression avant étalonnage	: 180 bars
- Pression après étalonnage	: 175 bars

Composé	Concentration du fabricant (nmol/mol)	Incertitude du fabricant (nmol/mol)
Benzène	15,0	10 %
Toluène	15,0	10 %
Ethylbenzène	15,0	10 %
p-xylène	15,0	10 %
m-xylène	15,0	10 %
o-xylène	15,0	10 %

2. CONDITIONS D'ETALONNAGE

2.1. MELANGE GAZEUX ETALON

Le mélange gazeux étalon est obtenu par dilution dynamique de mélanges gazeux de référence gravimétriques haute concentration fabriqués au LNE.

Composé	Identification du mélange de référence gravimétrique utilisé pour l'étalonnage de la bouteille n° 620064
Benzène	BEN/N2 0036
Toluène	TOL/N2 0028
Ethylbenzène	EBEN/N2 0015
p,m,o-xylène	OMP-X/N2 0008

2.2. INSTRUMENTS UTILISES

- Salle climatisée 21 °C ± 2 °C
- Débitmètres MOLBLOC 5 l/min et 100 ml/min à 273,15 K et à 1013,25 hPa
- Chromatographe INTERSCIENCE Compact GC (CHR 0023)
- Le manodétendeur livré avec la bouteille n'a pas été utilisé pour réaliser l'étalonnage.

suite du certificat page suivante

LNE

2.3. METHODE DE MESURE

L'analyse du mélange gazeux est effectuée par chromatographie en phase gazeuse avec détection à ionisation de flamme selon le mode opératoire suivant :

- ✓ Analyse du mélange gazeux à titrer ;
- ✓ Analyse du mélange gazeux étalon ;
- ✓ Analyse du gaz de dilution.

Les concentrations des composés analysés pour le mélange gazeux sont calculées à partir des surfaces des pics obtenus pour le mélange gazeux à titrer, le mélange gazeux étalon et le gaz de dilution et de la concentration du mélange gazeux étalon.

3. RESULTATS

Le résultat de l'étalonnage est reporté dans le tableau ci-après.

Etalonnage réalisé par :	Laurent SARAGOZA
Etalonnage réalisé le :	06/09/2016
N° d'identification :	620064

Constituant	Concentration mesurée (en nmol/mol)	Incertitude élargie (en nmol/mol)
Benzène	14,00	0,16
Toluène	13,53	0,16
Ethylbenzène	12,92	0,16
p-xylène	13,69	0,20
m-xylène	13,82	0,20
o-xylène	13,26	0,19

suite du certificat page suivante

4. INCERTITUDES

Les incertitudes élargies mentionnées sont celles correspondant à deux fois l'incertitude-type composée. Les incertitudes-types ont été calculées en tenant compte des différentes sources d'incertitudes, étalons de référence, moyens d'étalonnage, conditions d'environnement, contribution de l'instrument étalonné, répétabilité...

Ce certificat d'étalonnage garantit le raccordement des résultats d'étalonnage au Système International d'unités (SI).

fin du certificat d'étalonnage

ERLAP

Participating Laboratory	Joint Research Centre Ispra					
Acronym	ERLAP					
Person(s) responsible	Richard Connolly ,Pascual Perez Ballesta					
Contact e-mails:	pascual.ballesta@jrc.ec.europa.eu, richard.connolly@jrc.ec.europa.eu					
Telephone contact:	_+39033278-(5322) (5353)					
Characteristic of your BTEX analyser						
Trademark	Agilent + Markes TD					
Model:	7890A + Unity Air 2					
Version:						
Year of manufacture:	2012					
	Helium	Nitrogen	Hydrogen	Carbon dioxid	Air	
Carrier gas:	yes	yes	yes		yes	
Other gases used:						
Operating system:	Windows XP					
Cycle time, min:	30 min					
Adsorbent material:	TENAX GR, Carbopack B, CARBOPACK X, CARBOPACK C					
Sampling control	Pump/MFC					
Sampling temperature, °C	Ambient					
Sample volume, ml	200mL (20-800 ML)					
Number of adsorbent tubes	1					
Desorption temperature, `	300					
Desorption time, sec	180					
Desorption flow, ml/min	20					
Cryo-trap detail	Markes	Air Toxics, special preperation				
Trapping temperature, °C	-25					
Desorption temperature, °C	300	Desorption time, sec	180			
Desorption flow, ml/min	20	split flow, ml/min				
Stripper column						
Analytical column	J&W DB-1					
phase:	Dimethylpolysiloxane					
length, m:	50					
diameter (ID) mm:	0.32					
thickness (µm):	1.2					
analytical conditions:	50°C hold 5min., 12°C/min. to 150°C hold 5min., 75°C/min. to 200°C hold 5min.					
Traceability of your calibration Standard						
Certified reference material (CRM):	Primary Reference Gas Mixture					
Certified by	NPL					
Certified number:	Cylinder Number D386674					
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)				
Benzene	3.99	±0.08				
Toluene	3.99	±0.10				
Ethyl-benzene	3.99	±0.10				
m+p-Xylene	7.98	±0.20				
o-Xylene	3.97	±0.10				
Other methods						
Dilution of CRM						
Static Injection						
Permeation						
Additional comments						
sampling volume during the exercise 200 ml.						
multipoint calibration with volumes ranged from 20 to 800 ml						

ERLAP

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS REFERENCE MATERIALS 4002

PRIMARY REFERENCE GAS MIXTURE

Cylinder Number: D38 6674

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: **European Commission – Joint Research Centre**

ADDRESS: Institute for Environment and Sustainability, Via E. Fermi, 1, I-21020 Ispra (VA), Italy

CALIBRATION DATE: 29 June 2016

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Benzene	3.99 ± 0.08
Toluene	3.99 ± 0.10
Ethylbenzene	3.99 ± 0.10
m-xylene + *p*-xylene	7.98 ± 0.20
o-xylene	3.97 ± 0.10
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2016040285 **Date of issue:** 1 July 2016

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognise the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

List of abbreviations and definitions

AAA	Environmental Protection Agency (Lithuania)
AQUILA	air quality reference laboratories
BTEX	benzene, toluene, ethyl-benzene, xylene
CG	gas chromatograph
CHMI	Czech Hydrometeorological Institute (Czech Republic)
D.D.	Dynamic Dilution
DLI	Department of Labour Inspection. Ministry of Labour and Social Insurance (Cyprus)
EEA	Executive Environment Agency (Bulgaria)
EC	European Commission
EKONERG	Energy and Environmental Protection Institute (Croatia)
EPA	Environmental Protection Agency (Ireland)
ERLAP	European Reference Laboratory of Air Pollution
EU	European Union
U %	Relative Expanded Uncertainty
FID	flame ionization detector
GIOS	Chief Inspectorate of Environmental Protection (Poland)
H.C.	hydrocarbons
HMS	Air Quality Reference Centre, Hungarian Meteorological Service (Hungary)
ISCIII	Instituto de Salud Carlos III (Spain)
ISO	International Organization for Standardization
LCSQA	Laboratoire Central de Surveillance de la Qualité de l'Air (France)
LIKZ	Laboratory Croatian Hydrological and Laboratory Service (Croatia)
LV	limit value
QAQC	quality assurance quality control
n.a.	not available
NPL	National Physical Laboratory (United Kingdom)
NRL	National Reference Laboratory
PID	photo ionization detector
ppb (m/m)	part per billion, molar fraction
Press. Cyl.	pressurised cylinder
REE	Agency Ricardo Energy and Environment (United Kingdom)
RSD	Relative standard deviation, %
Tr. Std.	travelling standard
VMM	Vlaamse Milieumaatschappij, (Belgium)
$\overline{C}$	average concentration value
$\overline{C}_i$	average concentration value of I measurements

$\overline{C}_n$	average concentration for the step number n
$C_{n,\Delta t}$	concentration reported by the laboratory for the step n during the specified Δt : (0-30min), (30-60min) or (60-90min)
$\overline{\overline{C}}$	inter-laboratory average concentration
$\overline{C}_i^*$	robust average value
$C_{i,0-30\min}$	average concentration for the
C_{ref}	reference concentration value
C_8	refers to hydrocarbons with 8 atoms of carbon
E_n	$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$
k_i	Mandel-k value for laboratory i
n	number of replicated analysis
p	number of participating laboratories
P(Z)	probability function of the random variable Z.
R_c	residuals of the linear regression $\overline{C}_i$ vs C_{ref} at the evaluated concentration level, C
s^*	standard deviation of the robust average value $\overline{C}_i^*$
s_{bias}	standard deviation of the bias, $\overline{C}_i^* - C_{ref}$
$S_{\overline{c}_i}$	standard deviation of the average inter-laboratory value
s_i	standard deviation of the sample i.
s_L^2	inter-laboratory variance or between-laboratory variance
S_{LN37}	$s_{L_{N37}} = \sqrt{\hat{\sigma}_{N37}^2 - \frac{s_r^2}{n}}$: between laboratory standard deviation from the prescript conditions of proficiency assessment of AQUILA network.
s_r^2	repeatability variance or intra-laboratory variance
s_R^2	reproducibility variance
u	uncertainty of the method
u_{Cref}	uncertainty associated with the reference concentration value C_{ref}
$u_{n,\Delta t}$	uncertainty reported for concentration at the step n during the specified Δt : (0-30min), (30-60min) or (60-90min)
U_n	expanded uncertainty associated with the concentration calculated for the step n
$\mu g/m^3$	micrograms per cubic meter
α	level of significance

γ	$\gamma = s_R/s_r$, gamma value
σ	standard deviation
$\hat{\sigma}$	standard deviation for proficiency assessment
$\hat{\sigma}_m$	$\hat{\sigma}_m = \sqrt{(0.5 \cdot s_L)^2 + \frac{s_r^2}{n}}$: minimum standard deviation of proficiency assessment coherent with method reproducibility
$\hat{\sigma}_{N37}$	standard deviation for proficiency assessment prescript by AQUILA network
(1-α)	confidence level

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KJ-NA-28692-EN-N

JRC Mission

As the science and knowledge service of the European Commission, the Joint Research Centre's mission is to support EU policies with independent evidence throughout the whole policy cycle.

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